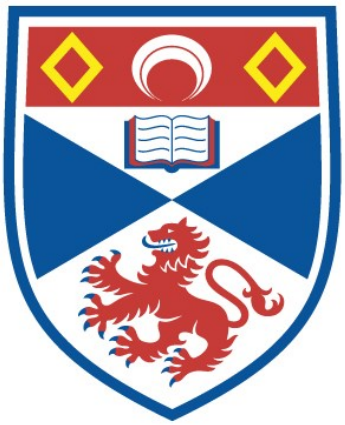
# THE STATISTICAL ASPECTS OF BOLTZMANN'S H-THEOREM

Christopher D. Green

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1954

# THE STATISTICAL ASPECTS OF BOLTZMANN'S H-THEOREM

being a thesis presented by

Christopher D.Green, B.Sc.

to the University of St Andrews
in application for the degree of
Doctor of Philosophy.

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STATEMENT

of the degree of collaboration between Dr ter Haar (DTH) and C.D.Green (CDG) concerning the content of the latter's thesis.

The subject and content of the thesis was suggested by DTH, as was also the basic method of approach.

Chapter I. Compiled by CDG from various sources.

Chapter II. Suggested by DTH and largely drawn from the papers referred to. Section 3 is largely due to DTH.

Chapter III. The application of the methods of Section 2 to this problem is due to CDG. The initial postulates and the various ways of approximating to facilitate the calculation are due to DTH.

Chapter IV. All CDG, apart from the matter of equnn.(4.307) to (4.309) which was suggested by DTH to prove that $\Sigma f_v \ln f_v^e$ = constant.

Chapter V. Again CDG, apart from some suggestions of DTH with regard to equation (5.108).

Chapter VI. CDG, apart from equation (6.110) and the proof of reversibility, both DTH.

Appendix. Procedure for evaluating the integral in section 3 was suggested by Dr J.A.Green.

## DECLARATION

I hereby declare that the following thesis is based upon research work carried out by me, that the thesis is my own composition and that it has not previously been presented for a higher degree.

The research has been performed in the Department of Natural Philosophy of the United College of the University of St Andrews under the supervision of Dr D. ter Haar.

CERTIFICATE

I certify that Christopher D. Green has spent nine terms engaged in research in the Department of Natural Philosophy of the United College of the University of St Andrews under my direction, that he has fulfilled the conditions in Ordinance No. 16 (St Andrews) and that he is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

5-8-54

## PERSONAL PREFACE

I matriculated in the United College of the University of St Andrews in October 1947 and followed the course leading to graduation with the degree of B.Sc. with Second Class Honours in Applied Mathematics in June 1951. In October 1951 I commenced research in the Department of Natural Philosophy of the same College under the supervision of Dr D. ter Haar, Lecturer in Theoretical Physics in the University of St Andrews. It is the result of this research that is presented now as a thesis in application for the degree of Ph.D.

## SUMMARY

This thesis is concerned with the consideration of the H-theorem in a statistical manner and the information that may be derived from it as to the variation with time of an isolated mechanical system, and especially the approach to equilibrium. A historical introduction is given in which it is shown how the need for such a statistical approach arose, and how the question of the behaviour of the fluctuations about the values of H predicted by the unrestricted H-theorem became important. The type of behaviour suggested by the Ehrenfests is quoted, and to verify this it is found to be necessary to consider in detail actual models.

Two classical models, the urn model and the wind-wood model, are considered, and then the procedure is generalized so as to include the whole class of models of the type consisting of two groups of particles, the one group moving and interacting with the members of the second group which are fixed. The transition probabilities and the rate of change of H, and the mean time of recurrence of a fluctuation are found for these models by considering the influence of fluctuations upon the Stosszahlansatz values for the numbers of collisions. The results confirm the postulates of the Ehrenfests. In addition light is thrown upon some of the basic assumptions common to the statistical treatment of collision processes.

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# Chapter I

## §1. The Historical Development of the H-theorem.

The development of statistical mechanics, as it was later dubbed by J.W.Gibbs, originated in the pioneering work of Kronig, Clausius, Clerk Maxwell and Boltzmann. It reached a significant landmark in the formulation by Boltzmann in 1872 of the famous H-theorem. This early work was concerned almost entirely with the statistical mechanics of the kinetical theory of gases, but the intensive investigation carried out subsequently on the validity of these first principles paved the way for later developments including the introduction of quantum mechanics into the framework of statistical mechanics which was found to be possible in a particularly direct manner. The value in fact, of the H-theorem as a fundamental of statistical mechanics may be judged by the way in which it is taken over into quantum statistics without essential change, and indeed in its statistical form it is peculiarly suited to the quantum approach. Boltzmann's later work on the ergodic theorem and the investigations into the symmetry of the equations of motion with respect to positive and negative time mark the closing stages of this first phase of the development. It was left to Gibbs (1902) to initiate a new phase with the introduction of ensemble theory, and the striking

generalizations which followed from it. Since the rise of the quantum theory more recently a third phase has become apparent, where the work of Boltzmann and Gibbs is considered anew in the light of the quantum postulates. In each of these stages the H-theorem has maintained its prominent position, thus supporting the contention of Tolman (1938) who holds it to be the most significant achievement of Boltzmann's entire work. It is therefore of interest to discuss in more detail the history of this theorem.

The early work of Clausius and Krönig on the kinetic theory of ideal monatomic gases assumed that the magnitudes of the velocities of the different atoms were constant and that the state of the gas could be defined by the collective of their directions of motion. From this Clausius (1858) was able to deduce the mean free path of a molecule in terms of its diameter and the gas density. Maxwell (1860) generalized this treatment to the extent of allowing the molecules to have different velocities and thus different energies, and studied the distribution of the energy amongst the molecules. This led to the celebrated result that the distribution law is of the same form as that which governs the distribution of experimental observations subject to random errors. Moreover, such a distribution is stationary with respect

to further collisions. The appearance of this characteristically statistical distribution and its association with random processes is significant.

Up to this point only the kinetic energy had been involved, and Boltzmann (1868) carried the work a stage further by using a method of considerable mathematical elegance to include the internal potential energy of multi-atomic molecules and also the effect of external applied fields of force. He was able in this way to show that a quantity E (later denoted by H) defined by the numbers of molecules contained in the various elements of phase space would continuously decrease due to collisions to a minimum value. At this minimum the distribution is that given by Maxwell's Law, and is stationary, so that $dE/dt \leqslant 0$. The quantity E was defined as an integral

$$E = \iiint f \ln f \, du\,dv\,dw \quad , \qquad (1.101)$$

where u, v and w are components of velocity, and the distribution function f depends on velocity and time. As defined here E is continuous, but at one stage Boltzmann treated the integrals involved as the limiting cases of sums, and thus in effect quantized the energy field to obtain the same result in the limit. There is of course no suggestion that he intended anything more

than the simplification of the analysis by this method, though it is tempting to speculate on the intuitive insight he might have had into the quantum method. In a later paper on the probability basis of the H-theorem Boltzmann (1877) uses the same method, but again it is merely to simplify the mathematics involved in calculating the probability of a system containing a large number of constituents.

Boltzmann regarded the H-theorem as proving by the rigorous methods of mechanics the Second Law of Thermodynamics which had hitherto been in the nature of an assertion. He demonstrated the correspondence between the quantity H (as E was now called) and the entropy defined by $\int dQ/T$. He also asserted that the hypotheses put forward by Clausius and Maxwell in their work were sufficient to give a self-consistent explanation of irreversible processes, and in particular of the one sided increase of entropy with time. The hypotheses referred to are of great interest because they lie at the foundations of statistical mechanics, and upon their reasonableness the validity of the whole structure depends. The Ehrenfests (1911) in their valuable review of this whole subject formulate these as follows:

(1) The Hypothesis of Mechanical Structure. Every body of gas is a mechanical system consisting of

enormously many molecules of similar types and of fixed (or nearly fixed) structure.

(2) The Probability Hypothesis. The combined motions of these molecules are so complicated that they cannot be followed individually, but they can be described as conforming to probability laws referring to the relative frequencies of occurrence of different configurations and motions.

## §2. Mechanics and Probability.

Since thermodynamics is most successful in dealing with equilibrium situations we would expect statistical mechanics to give some sort of explanation of this. The H-theorem is an assertion concerning the equilibrium situation for it states that whatever the initial state of a system, under the influence of conservative forces it will move towards the equilibrium state with the increase of time. This equilibrium state is a steady one, and once it is reached it is preserved. If then, as is the case, the relaxation time necessary to reach this state is relatively small, then we will be mainly concerned with the equilibrium situation. It is therefore of interest to have a knowledge of the length of this relaxation time, especially in the light of the following discussion.

We now come to the two famous objections to the H-theorem which stem from the first hypothesis of the preceding section. The first is Loschmidt's Reversibility Paradox (1876). According to the H-theorem we should expect in an isolated system that the value of H would continually decrease with time until a minimum were reached after which it would remain constant. However, according to the principle of dynamic reversibility of classical mechanics it is as equally possible for any internal behaviour of an isolated system to take place as its reverse. Since it is postulated by hypothesis (1) that the derivation of the H-theorem follows the canons of classical mechanics it is evident that it should be subject to this effect. But if H decreases steadily as t increases then in the reverse motion it would increase, thus producing a contradiction. In physical terms, such a system is just as likely to diverge from equilibrium as to approach it.

Secondly we have Zermelo's Recurrence Paradox (1896). This is based upon a theorem due to Poincaré which states that an enclosed, isolated mechanical system will perform some sort of periodic motion if undisturbed. We define the state of the system consisting of N complex molecules each with s degrees of freedom, described by the 2sN generalized coordinates $(q_1,\ldots,q_{sN},p_1,\ldots,p_{sN})$, as

given by a point in 2sN-dimensional phase space. We call this $\Gamma$-space; the q's and p's are space and momentum coordinates respectively. Each possible state of the system is then characterized by a point in phase space, and since the system is enclosed the total extension of phase space available for such a representative point is finite. The theorem then states that after a finite, though possibly very long , time the representative point of the system will always return to positions in phase space which are as close as we may wish to define to positions where it has been already. In other words the system is periodic to within any specified degree of accuracy, or quasi-periodic. From this it follows that any given value of H however large will recur again after a finite time, thus contradicting the H-theorem once more from a mechanical standpoint.

The production of these two paradoxes gave rise to an immense amount of discussion concerning the validity of the H-theorem and of the statistical-mechanical method, which had the good result of leading to an appreciation of the part played by probability in this method. It is perhaps as well to mention here that although the H-theorem as originally derived applied only to certain gas models, later work by Boltzmann (1875) achieved the derivation with general reference to the forces involved,

for example gravitational or electromagnetic fields, friction and so on. In this case however it is necessary to know the exact nature of the forces if we are to determine the rate of approach to equilibrium.

The fundamental necessity for the resolution of these paradoxes is the realisation of the probability nature of the mechanics we are using. Boltzmann's work showed clearly when he found that it was necessary in order to perform the calculations to divide the total volume of phase space into very small but still finite elements. In the case we have mentioned already, for example, the velocity range (or the energy range) was divided into equal, discrete intervals. Decreasing the size of these in order to transform sums into integrals can only be performed under the restriction that each element will still contain, on the average, very many particles (Boltzmann 1877). If this is not done then we find that we need completely detailed information about the motion of each particle, which would bring the whole calculation back into the realm of classical mechanics, but with enormously many equations of motion to be solved. In order then to use statistical methods we must make some sort of probability statement concerning these phase cells. This leads directly to the question of the Stosszahlansatz.

§3. The Stosszahlansatz.

This expression, due to Boltzmann and by common consent retained in its original form, denotes in principle any assumption at all about the number of collisions. In practice it has become associated with the particular assumption that Boltzmann himself used so often. In general terms this was that each cell or element in phase space contained very many particles, and that the volume of each cell was so small that merely the averages taken over the cells were sufficiently exact. This is the same as the assumption of molecular chaos ( compare Jeans, 1921 and Fowler, 1936). The actual assumption is that the probability of finding a particular distribution of velocities is independent of the position of the phase cell but depends only upon its volume. Thus the chance of finding a molecule in the cell dxdydzdudvdw is

$$\nu f(u,v,w)\, du dv dw\, dx dy dz , \qquad (1.301)$$

where f is the distribution law for the velocities of a group of molecules in a small volume $\Omega$ which contains the cell dxdydz. $\nu$ is the density. We assume this to be true for all elements of volume dxdydz wherexver they may be situated. This assumption means that if we have two classes of molecules in the volume $\Omega$ which are to collide with each other, then there will be no

influence on the distribution of the second class due to our previous assertion regarding the first.

When actually performing calculations on the number of collisions taking place between the two classes of molecules Boltzmann used the assumption in the following manner. One calculates the sum of the volumes of the cylinders which the molecules of the first class sweep out in their motion relative to the second class in the time interval $\Delta t$. The number of collisions that occur in $\Delta t$ is then given by the number of molecules of the second class that is contained within this volume. The value is thus

(swept-out volume).(number of mols. of the 2nd class/vol)

In this case the Stosszahlansatz is that the probability of finding a molecule of the second class in a unit volume is the same everywhere in the gas. Once this assumption has been made the continuous decline of H follows by exact mechanical reasoning. It must be borne in mind however, as the Ehrenfests (1911) have pointed out, that this assumption is in effect an averaging of the positions of the molecules over all their possible distributions within the elementary volumes. We have calculated the average or the most probable number of collisions in $\Delta t$, and it therefore follows that any statements we derive from this about the variation of H

due to collisions must partake of the nature of probability statements. The H-theorem then appears in its restricted form as:

If it is highly probable that the Stosszahlansatz is justified, then it is highly probable that $dH/dt \leq 0$ for all times.

This approach as we will see later will dispose of the difficulties produced by the mechanical paradoxes. There is a further point advanced by the Ehrenfests. This is that H will not be a continuous variable at all, but a discrete one. The manner in which H is defined renders this evident, for it is a function of the numbers of molecules which are contained in the various cells in phase space. Since these cells are now taken to have finite extension the occupation numbers will change due to collisions in a discrete manner, while there is also the possibility of collisions which do not alter the occupation numbers and even of quite different collision processes which give rise to the same distribution. We do not therefore have a detailed knowledge of the processes involved even if we know the occupation numbers at all times, but instead an approximation whose extent depends entirely upon the size of the cells. In the limit as the volume of the cells tends to zero so does the number of collisions as given by the Stosszahlansatz tend to the

actual value. Under the above assumption we may approximate to this by the average taken over each cell, so that H is a discrete variable with what might be termed a 'coarseness' depending on the cell volumes.

If we are to say that the Stosszahlansatz represents taking the most probable number of collisions then it is reasonable to suppose that the true number of collisions fluctuates in a random manner about this value as an average. This is not necessarily true, but evidence from the study of brownian motions and thermal fluctuations indicates that it is at least very plausible. In this case H would be given as a discrete function of these discrete stochastic variables, the actual collision numbers. H is then itself liable to fluctuations, and one of the main aims of this dissertation is to calculate their extent and behaviour. The restricted H-theorem in its probability form states that the most probable variation in H with increasing time is a decrease to a minimum. But we may say now that fluctuations will take place around the average values and that any value of H is possible at any time, although such values may have vastly different probabilities of occurrence. In order to satisfy the triple requirements of the H-theorem, the reversibility paradox and the recurrence paradox the variation of H with time must manifest the following

behaviour;

(1) The probability of the value of H decreasing at any time must be greater than that of it increasing, so that overall H tends downwards to a minimum.

(2) The plot of H against time will show a series of peaks and valleys. This is because H must rise and fall with equal frequency so as to be reversible with respect to time.

(3) The probability of the recurrence of any value of H however large must be finite, although it may be very small especially for values greatly different from the minimum one.

In addition one would expect any such large fluctuations to be very improbable indeed, and very short lived, since they are not observable in nature as far as is known. Small fluctuations in the neighbourhood of equilibrium might be much more likely.

Such a curve as this would appear at first sight to be geometrically at least, highly unlikely, and when its existence was first postulated by Boltzmann much doubt was expressed as to its feasability. Nevertheless the Ehrenfests (1907) by the consideration of a simple lottery model ( the Urn Model ) constructed what they called the $\Delta$-curve, which satisfied all these conditions. This model is discussed in Chapter II. We intend to show in

succeeding chapters that such behaviour is also exhibited by a class of simple mechanical models and to give quantitative results for the average times of recurrence of such states of fluctuation. The class is question is that of models containing two sets of particles, the one set being fixed and the other colliding with them. In this way one is able to investigate the propriety of von Smoluchowski's definition (1912) of an irreversible system as that of a system appearing to be irreversible only when the times available for its observation are much less than the average time of recurrence in the system.

## §4. Probability and Ensembles.

By the use of probability methods it is possible to extend the familiar connection between entropy and the quantity H, that is

$$S = -kH \quad , \tag{1.401}$$

which is valid at equilibrium, into a similar definition of S which will be valid in all situations. The method relies of course on the division of phase space into cells as already explained. We suppose that $2s$ -dimensional $\mu$ -space is subdivided into small but finite cells of equal volume $\omega$ , and which we denote by $\omega_1, \omega_2, \ldots$ . Each complex molecule of the system under consideration will be

represented by a point in $\mu$-space. The number of such points is N, and we assume that the numbers in each cell, $N_1, N_2, \ldots$ are on the average large as compared with unity. The situation Z described by a point in $2sN$-dimensional $\Gamma$-space is thus defined by the collective of the occupation numbers $N_i$. Although to every point in $\Gamma$-space there corresponds one situation Z, yet to each situation Z belong many points in $\Gamma$-space because of the freedom of the representative points to range throughout the interiors of the cells $\omega_i$ without altering Z. Furthermore any permutation of these points amongst the cells leaves Z unchanged. Thus for each Z there is a volume in $\Gamma$-space all points of which belong to the situation Z, and the volume of this so-called Z-star is given by W(Z) where

$$W(Z) = \frac{N!}{N_1! N_2! \ldots} \omega^N \quad . \qquad (1.402)$$

The validity of this expression depends upon the assumption of equal a priori probabilities of finding a representative point in any cell, and if the cells should have different volumes, that the probability should be proportional to the volume. If this is so then W(Z) when suitably normalized by a constant factor gives the probability of a state Z. The maximum of W(Z) consistent with the conservation of the total number of particles, the energy and the momentum is then found ( e.g. see ter Haar, 1954, ch. II ) to give the Maxwell-Boltzmann equilibrium

distribution. Remembering that the $N_i$ are large numbers we may write

$$-\ln W(Z) = \sum_i N_i \ln N_i + \text{constant} \\ = H(Z) + \text{constant} , \tag{1.403}$$

according to Boltzmann's definition of H. Therefore we have a definition of entropy for all situations

$$S = k \ln W(Z) . \tag{1.404}$$

The H-theorem will then give to the Second Law the meaning of the likelihood of the progress of a system from less probable states to the most probable one, the equilibrium state. Regarded in this light the choice of H has a much clearer significance than merely that of a positive function of the occupation numbers.

In the above discussion the equilibrium state has appeared as being the most probable one. It is also possible to define it as an average. For example it is the time average of all states, because whatever the initial state may have been, after a comparatively short relaxation time the system will have reached equilibrium and will remain there for the rest of time apart from short lived fluctuations. These two definitions of the equilibrium state are important because it is possible to show that the Maxwell-Boltzmann distribution satisfies them both and that therefore they are equivalent. The Maxwell-

Boltzmann distribution corresponds to the Z-star of the largest volume, and W(Z) decreases rapidly as soon as Z departs from this distribution. If a certain assumption is made then it can be shown that over the full extent of time the Maxwell-Boltzmann distribution will be realized most of the time so that it is also the average distribution. Thus the H-theorem shows that the Maxwell-Boltzmann distribution is in fact the equilibrium one, while any other distribution will tend towards this one and will remain there for the vast majority of time. The assumption which has to be made is that the system is ergodic - that is to say, that the representative point in $\Gamma$-space will in time pass through every point on the energy surface $E(p,q) = E$ which is a $2sN-1$ dimensional hypersurface in $\Gamma$-space. This assumption is not entirely justified since it has been proved that true ergodic systems do not exist. However quasi-ergodic systems do exist, such that the orbits will recur arbitrarily close to any point. We have encountered this already in connection with the Poincaré cycle. The question of the ergodic theorem has given rise to a great deal of discussion since the time of Boltzmann, and the matter cannot be considered to be completely understood even now.

Another average may be defined if we consider the ensemble of systems of similar structure and which at the

initial time t=0 have states Z each of which belongs to the same Z-star. The collective of these systems forms a micro-canonical ensemble in the Gibbsian sense if the total energies lie within the bounds E and E+dE. At any time the average taken over the whole ensemble will give the value of H predicted by the unrestricted H-theorem which is to say that although most of the systems will obey this theorem fluctuations cause the rest to deviate from it. The average behaviour of the system under consideration is then given by the average taken over the whole ensemble. This was Boltzmann's method of defining the average behaviour and is the one that we will be using here. This is not the only way for we can also redefine H in accordance with the Gibbs treatment. Previously H was defined directly for the system of interest and not for the whole ensemble. The Gibbs method introduces a function which refers to the whole ensemble and not just to one part of it. This function is variously denoted, and we use the form $\bar{\bar{H}}$ following Tolman (1938). The earlier definition of H in the form $H = \int f \ln f \, d\omega$, indicates that H is the mean value of $\ln f$ taken over the system. $\bar{\bar{H}}$ is taken analogously as the mean of the logarithm of the coarse-grained density taken over the ensemble. It then follows that $\bar{\bar{H}}$ decreases steadily with increasing time until it reaches a minimum. Such a

minimum in this case corresponds to an only approximately uniform distribution due to the fact that we have used the coarse-grained probability. In this event the procedure deals with macro-canonical ensembles and is especially suitable for the quantum statistics. In all the models which we consider the classical statistics are adhered to so that the Boltzmann method will be sufficient.

For these ensembles it is possible to show that the time average of H is the same as the state average so that there is no ambiguity about the equilibrium state. The relation between H and $\overline{H}$ is of the form

$$\overline{H} = H + \text{constant} . \qquad (1.405)$$

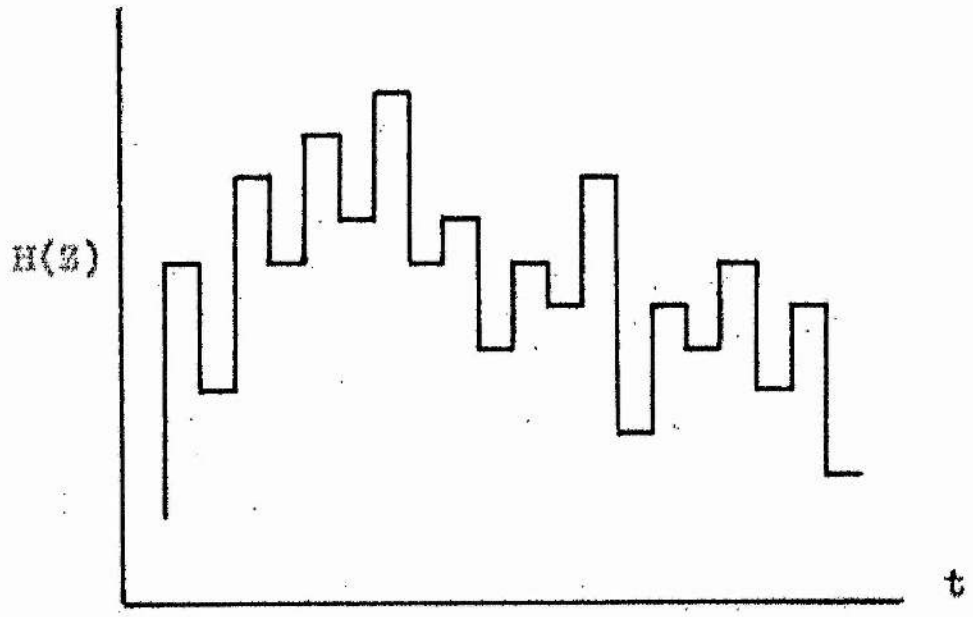
Among the applications of this method is a justification of the use of micro- and macro-canonical ensembles for the description of real systems on the grounds of the applicability of the results ( e.g. ter Haar, 1954, App.1).

## §5. The Ehrenfests' Programme.

In their article on the foundations of statistical mechanics the Ehrenfests (1911) gave a programme of results which apparently follow from the consideration of the H-curve by statistical methods. It is the purpose of this dissertation to apply some of the points of this programme to the class of mechanical models that we have mentioned already in order to see to what extent they are

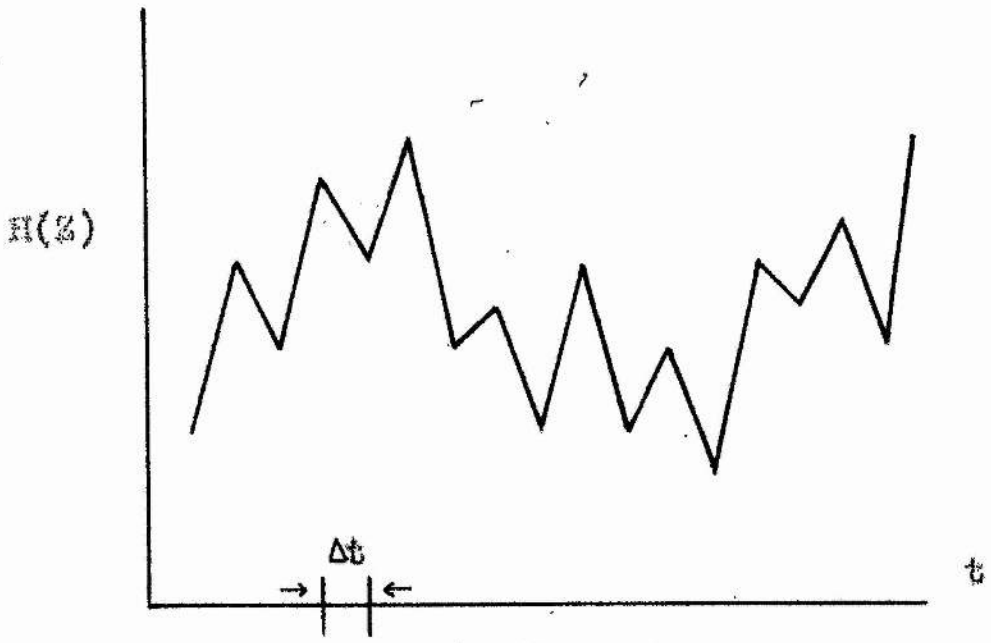
justified. In this way it is hoped to demonstrate the validity of the conclusions quantitatively, for at least simple mechanical models, which should be of value since it is extremely difficult to give general treatments of such subjects. The previous section gives many examples of this where the argument is frequently interrupted by assumptions which, although they are exceedingly plausible, remain unproved assumptions nevertheless. An investigation of this sort was apparently intended by the Ehrenfests, but as far as we know no model more complicated than the Urn Model discussed in Chapter II has been treated in this way although some of the work done on brownian motions is very similar.

The discussion in future chapters will centre on the behaviour of the H-curve. The time variation of H is due to the transfer of representative points from one cell in $\mu$-space to another, so that the curve of H with respect to time will be a discontinuous step function as is illustrated in figure 1. We construct from this step function the H-curve by dividing the time abscissa into equal elements $\Delta t$, each of which is so short that it is small as compared with experimental time intervals yet still large enough for many collisions to take place during it ( figure 2 ). This is exactly analogous to the division of phase space into cells, and is equally




H as a function of time.

Figure 1




The H-curve.

Figure 2

justified although in the same way it gives rise to problems which will be discussed later. We then pick out from the step function a discrete set of points which are separated by time intervals $\Delta t$ and plot these against time to form the H-curve. The time is then measured in multiples of $\Delta t$. The Ehrenfests' programme demands that the H-curve should satisfy the following requirements:

(1) If H' is much larger than $H_{min}$ then the H-curve will practically always decrease from H'. This must also be true if the time direction is reversed. The H-curve should practically always be in the neighbourhood of $H_{min}$. $H_{min}$ denotes the minimum ( equilibrium ) value of H.

(2) Despite this any value of H must recur again and again in accordance with Poincaré's quasi-periodic motion, but in order that the process appear irreversible the mean time of recurrence of a value of H appreciably different from $H_{min}$ should be so large as to be outside the range of observation. Hence the magnitude of such a mean time will give an indication of the reversibility of the process.

(3) Suppose that the situation at a time $t_A$ is described by points lying in a Z-star of volume $W(Z_A)$, where $H(Z_A)$ is considerably larger than $H_{min}$. The ensuing motion will be different for the representative points of the systems of the ensemble which defines the $Z_A$-star. If we consider

the separate H-curves of each member of the ensemble they should have the following properties. Firstly if $\eta_n$ denotes the average over the ensemble of all the H-values at a time $t_A + n\Delta t$ then the dispersion of the various H-values around this average will be very small. Secondly the curve of $\eta_n$ with respect to time will decrease monotonically to $\eta_{min}$ and remain there. That is to say that the averages of the H-values at succeeding times obey the unrestricted H-theorem, so that the $\eta$-curve and the H-theorem curve are the same.

If the behaviour is such as to satisfy these conditions then the conclusions mentioned in the previous section follow immediately.

The models with which we are concerned in the succeeding chapters are all of the simple type which consists of two classes of particle, the one fixed and the other moving and interacting with the first but not with itself. This type is sufficiently simple for the mathematics involved to be relatively uncomplicated and yet for there to be a reasonably wide range of physical application. The use of H as the function defining the state of a system ensures that the transition to physically observable conditions is, in principle, possible, which would not be so if we had used for example the collective Z. For all the models we consider it will be shown in

detail that these conditions are all satisfied. In view of the great difficulty in proving some of these results in general it was considered to be helpful towards a real understanding of the subject to show that such behaviour did indeed follow in a mechanical model from the abandonment of the original Stosszahlansatz and the consideration of fluctuations. In addition the quantitative application to the question of apparent reversibility would seem to be possible only in such a way as this.

# Chapter II

## §1. The Urn Model.

Boltzmann (1894) first introduced the idea of using a simple lottery as a mathematical model to illustrate the probability behaviour of the H-curve, and later this notion was taken up by the Ehrenfests (1907) who devised the now familiar urn model on similar principles. This has since attracted considerable attention both from physicists; for example the papers of Kohlrausch and Schrödinger (1926), who actually performed the lottery and whose results we use in this section, and Wang and Uhlenbeck (1945); and also from mathematicians such as Kac (1945,1947) and Bellman and Harris (1951) who find in it a useful testing ground for methods in the theory of chain processes. Here wexare not very closely concerned with such an unphysical model except for historical reasons and because of the close resemblance that it bears to the simplest mechanical model that we discuss. Most of the results of this chapter have appeared already in ter Haar and Green (1953).

The Ehrenfests' urn model is constructed in the following manner. Let N balls numbered from 1 to N be distributed between two urns A and B. In addition suppose there to be a box which contains N tickets also

numbered from 1 to N. At regular intervals of time a ticket is drawn at random from the box, its number noted, and is then returned and the tickets reshuffled. At the same time the ball which bears the same number as that on the ticket is removed from the urn in which it is and is transferred into the other. The introduction of the regular intervals of time, say $\frac{1}{2}\tau$ apart, is a slightly strained device to include a time scale, but it finds a good analogy in the mechanical models. The numbers of balls at any time in the urns A and B respectively are denoted by $N_A$ and $N_B$. Let the difference between these two numbers be denoted by $\Delta$, then

$$\Delta = N_A - N_B \quad \text{and} \quad N = N_A + N_B \ . \qquad (2.101)$$

If $\Delta = 0$ then the situation is an equilibrium one so that the modulus of $\Delta$ measures the departure of the system from equilibrium. As we will show, $|\Delta|$ reflects the behaviour of H in a mechanical system. If we consider the position after z draws have been made, that is after the lapse of a time $\frac{1}{2}\tau z$, and if z is large enough to ensure that the state $\Delta = 0$ shall have occurred at least once, then the initial distribution of balls over the urns will have no further effect and may be neglected. Suppose that after z draws urn A contains $N_A = \frac{1}{2}(N + \Delta)$ and urn B $N_B = \frac{1}{2}(N - \Delta)$ balls. Such a state could have occurred in two ways. After the (z-1)th draw there

could have been a state $\Delta-2$ or $\Delta+2$, since at each draw both $N_A$ and $N_B$ change by 1. In the first case $N_A = \frac{1}{2}(N+\Delta-2)$ and $N_B = \frac{1}{2}(N-\Delta+2)$, and for the state $\Delta$ to occur as the result of one draw then a ball must be moved from B into A. The probability of this happening is $(N-\Delta+2)/2N$ since the probability of any particular ticket being drawn is $1/N$. Similarly the probability of transfer from $\Delta+2$ to $\Delta$ is $(N+\Delta+2)/2N$.

Denoting the probability of the occurrence of the state $\Delta$ by the function $w(\Delta)$ we have

$$w(\Delta) = w(\Delta+2)(N+\Delta+2)/2N + w(\Delta-2)(N-\Delta+2)/2N. \qquad (2.102)$$

From equation (2.102) we may derive the series of relations

$$w(0) = w(2)(N+2)/2N + w(-2)(N+2)/2N$$
$$w(2) = w(4)(N+4)/2N + w(0)N/2N$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

Since $w(\Delta)$ is symmetric in $\Delta$ we obtain from these recurrence formulae the values of $w(\Delta)$ in terms of $w(0)$:

$$w(2) = w(0)\, N/(N+2)$$
$$w(4) = w(0)\, N(N-2)/(N+4)(N+4)$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$w(\Delta) = w(0)\tfrac{1}{2}N(\tfrac{1}{2}N-1)\ldots(\tfrac{1}{2}[N-\Delta]+1)/\tfrac{1}{2}(N+2)\ldots\tfrac{1}{2}(N+\Delta)\,.$$

Therefore

$$w(\Delta) = w(0)\frac{(\frac{1}{2}N)!\,(\frac{1}{2}N)!}{N!}\binom{N}{\frac{1}{2}[N+\Delta]} \qquad (2.103)$$

where $\binom{a}{b}$ is the binomial coefficient $\frac{a!}{b!(a-b)!}$. The expression for w(0) is found from the normalization condition

$$\sum_{-N}^{+N} w(\Delta) = 1 = \frac{(\frac{1}{2}N)!(\frac{1}{2}N)!}{N!}\, w(0)\, 2^N \quad . \qquad (2.104)$$

Combining equations (2.103) and (2.104) gives us the probability distribution of $\Delta$ as

$$w(\Delta) = (\tfrac{1}{2})^N \binom{N}{\frac{1}{2}[N+\Delta]} \quad , \qquad (2.105)$$

which is the formula for a Bernoulli distribution, with an average value of $\Delta$ as zero, the equilibrium value. If we assume $N \gg 1$ as it must be for statistical results to be applicable, then equation (2.105) may be written to a fair approximation in the gaussian form

$$w(\Delta) = (2\pi N)^{-\frac{1}{2}}\, e^{-\Delta^2/2N} . \qquad (2.106)$$

The diagram (figure 3) represents the subsequent behaviour of the system which commences in a state $\Delta$. After one draw has been made, that is after time $\frac{1}{2}\tau$, $\Delta$ may have one of the values $\Delta+2$ or $\Delta-2$, with the transition probabilities

$$p(\Delta,\Delta+2)=(N-\Delta)/2N \quad \text{and} \quad p(\Delta,\Delta-2)=(N+\Delta)/2N \quad . \qquad (2.107)$$

Each mesh in the net represents a possible change of $\Delta$, and it can be seen that after two draws (or a time $\tau$) there will be three possibilities: $\Delta+4$, $\Delta$ or $\Delta-4$. The total transition probabilities $w(\Delta,\Delta+4)$, $w(\Delta,\Delta)$ and $w(\Delta,\Delta-4)$ are then given by

Figure 3

$$w(\Delta,\Delta+4) = p(\Delta,\Delta+2)p(\Delta+2,\Delta+4)$$
$$w(\Delta,\Delta) = p(\Delta,\Delta+2)p(\Delta+2,\Delta) + p(\Delta,\Delta-2)p(\Delta-2,\Delta)$$
$$w(\Delta,\Delta-4) = p(\Delta,\Delta-2)p(\Delta-2,\Delta-4) \quad .$$

Using equations (2.107) we have

$$\left.\begin{aligned} w(\Delta,\Delta+4) &= (N+\Delta)(N+\Delta-2)/4N^2 \\ w(\Delta,\Delta) &= (N^2+2N-\Delta^2)/2N^2 \\ w(\Delta,\Delta-4) &= (N-\Delta)(N-\Delta-2)/4N^2 \end{aligned}\right\} \quad . \qquad (2.108)$$

Any $w(\Delta,\Delta')$ for which $\Delta-\Delta'$ is not equal to $+4$, 0 or $-4$ vanishes, so that we have contained in equations (2.106) and (2.108) all the data needed to describe the behaviour of this random walk process. From equation (2.108) it can be seen that for positive $\Delta$, $w(\Delta,\Delta-4)$ is greater than $w(\Delta,\Delta+4)$ so that a decrease is more likely than an increase. Since the average value of $\Delta'$ at time $t+\tau$, starting with $\Delta$ at t, is given by

$$\Delta'_{av} = (\Delta-4)w(\Delta,\Delta-4) + \Delta w(\Delta,\Delta) + (\Delta+4)w(\Delta,\Delta+4)$$
$$= \Delta - 4\Delta(N-1)/N^2 \quad , \qquad (2.109)$$

then the average rate of change of $\Delta$ will be

$$(d\Delta/dt)_{av} = (\Delta'_{av}-\Delta)/\tau = -4\Delta(N-1)/\tau N^2 \; ; \qquad (2.110)$$

which is certainly negative.

We defer until the next section the evaluation of the average recurrence time of a state $\Delta$ until we shall have derived the general formulae.

## §2. The Mean Life and Recurrence Times.

The formulae which we derive here and the method by which they are obtained are both due to Chandrasekhar (1943, ch. III, §1) who developed them during his study of brownian motions. Suppose that we have a chain process such as a random walk, which is defined by w(n) and w(n,n) where w(n) is the probability of occurrence of a state n and w(n,n) the probability that the state n will occur on two consecutive occasions a time $\tau$ apart. Let $\phi_n(k\tau)$ denote the probability that the same state n occurs on k-1 consecutive occasions but not on the kth. Then

$$\phi_n(k\tau) = [w(n,n)]^{k-1}[1-w(n,n)] \quad . \qquad (2.201)$$

The definition of the mean life time T(n) of the state n then follows naturally from that of $\phi_n(k\tau)$ with the equation

$$T(n) = \sum_{k=1}^{\infty} k\tau\, \phi_n(k\tau) \quad . \qquad (2.202)$$

Combining equations (2.201) and (2.202) and evaluating the sum we have

$$T(n) = \tau/[1-w(n,n)] \quad . \qquad (2.203)$$

The derivation of the average time of recurrence ⓗ(n) of a state n is performed in an analogous manner. Suppose that $\psi_n(k\tau)$ is the probability that starting with any state not equal to n (denoted by $\underline{n}$) then on k-1 consecutive occasions states $\underline{n}$ should occur, but that

on the kth occasion we have a state n. Then

$$\textcircled{H}(n) = \sum_{k=1}^{\infty} k\tau\, \psi_n(k\tau) \quad . \tag{2.204}$$

Let $w(\underline{n},\underline{n})$ be the probability of a transition from a state not n to any other state not n in time $\tau$. Obviously

$$\psi_n(k\tau) = [w(\underline{n},\underline{n})]^{k-1}[1-w(\underline{n},\underline{n})] \quad . \tag{2.205}$$

As before by combining equations (2.204) and (2.205) we obtain

$$\textcircled{H}(n) = \tau/[1-w(\underline{n},\underline{n})] \quad . \tag{2.206}$$

We next express $w(\underline{n},\underline{n})$ in terms of $w(n)$ and $w(n,n)$. Firstly it is evident that

$$1-w(\underline{n},\underline{n}) = w(\underline{n},n) \quad . \tag{2.207}$$

Secondly, at equilibrium the number of transitions from states not n to a state n must be equal to the number of transitions from the state n to states not n. Thus

$$[1-w(n)]\, w(n,n) = w(n)\, [1-w(\underline{n},n)] \quad . \tag{2.208}$$

Therefore

$$1-w(\underline{n},n) = \frac{[1-w(n,n)]\, w(n)}{1-w(n)} \quad . \tag{2.209}$$

Setting equations (2.209) and (2.207) in (2.206) and using the previously derived expression for $T(n)$ we have

$$\textcircled{H}(n) = T(n)[1-w(n)]/w(n) \quad . \tag{2.210}$$

The results of the previous section expressed in equations (2.106) and (2.108) may now be introduced directly into the formulae for $T(n)$ and $\textcircled{H}(n)$. The mean

life time of the state $\Delta$ is thus

$$T(\Delta) = 2N^2\tau/(N^2-2N+\Delta^2) \quad . \qquad (2.211)$$

If N and $N\pm\Delta$ can be assumed to be large as compared to unity then approximately

$$T(\Delta) \simeq 2\tau \quad . \qquad (2.212)$$

Under the same assumptions $w(\Delta)$ will be small compared to unity and so the average time of recurrence will be given approximately by equations (2.210) and (2.212) as

$$\Theta(\Delta) \simeq 2\tau/w(\Delta) = 2\tau(2\pi N)^{\frac{1}{2}} e^{\Delta^2/2N} \quad . \qquad (2.213)$$

The requirements (1) and (2) of the Ehrenfests for the H-curve are thus satisfied by the $\Delta$-curve of this statistical model. For large $\Delta$ equation (2.110) dictates a rapid probable decrease towards equilibrium. The process is obviously reversible with respect to time. The mean life of a state with small $\Delta$ is of the order of $2\tau$, but for greater deviations from equilibrium it will decrease as the power $\Delta^{-2}$. Furthermore the recurrence time of a state $\Delta$ increases in the same way. As an example we may consider the lottery performed by Kohlrausch and Schrodinger. Here N= 100, and 5000 draws were made. We will take $\tau$ =1 sec so that the total time occupied by the experiment would be 2500 sec. Then if $\Delta$ =40, which is less than half the maximum value, we find that $\Theta(\Delta)$ is $3.10^5$ sec, one hundred times greater

than the duration of the observations. Even for $\Delta = 1$, a one per cent deviation, $\Theta(\Delta)$ is still of the order of fifty seconds.

§3. The One-dimensional Wind-wood Model.

For our first mechanical model we take a variant of the Ehrenfests' wind-wood model in one dimension. The true model is treated fully in the next chapter, and we discuss this simple form here because of its similarity to the urn model. The main difference is that we now encounter the Stosszahlansatz and can therefore introduce fluctuations.

To describe the model we consider a line segment in the x-direction along which N point particles are moving in the positive and negative directions. We assume that these particles do not interact with each other and that they are all moving with the same constant speed c. Along the segment n 'screens' are randomly distributed in fixed positions, and they have the property that a point particle colliding with a screen has the probability $a$ of being reflected back, and of $1-a$ of passing through, in both cases without change of speed. We may say that the model corresponds in a very rough way to the electrons in a metal.

Let $f_1$ and $f_2$ be the numbers of particles moving in

the positive and negative x-directions respectively and let the difference between them be denoted by $\Delta$ so that (compare equation 2.101)

$$\Delta = f_1 - f_2 \quad , \qquad N = f_1 + f_2 \quad . \tag{2.301}$$

The probability $w(\Delta)$ is again a Bernoulli distribution so that if $N \gg 1$ both equations (2.105) and (2.106) are still true. In order to obtain $W(\Delta,\Delta')$ we must calculate the rates of change of $f_1$ and $f_2$. Let $x_1$ and $x_2$ be respectively the numbers of particles which during a time $\tau$ change their directions from the positive to the negative x-direction and vice versa. If we neglect end effects, and the possibility that a particle might change its direction more than once during $\tau$ , we have

$$df_1/dt = (x_2 - x_1)/\tau \,, \quad df_2/dt = (x_1 - x_2)/\tau : \quad d\Delta/dt = 2(x_2 - x_1)/\tau \tag{2.302}$$

If we choose $\tau$ to be so small that the distance travelled by a particle during $\tau$ is less than the mean free path amongst the screens, so that

$$\tau \ll 1/nc \quad , \tag{2.303}$$

then the possibility of second collisions during $\tau$ is negligible.

If we were to make a Stosszahlansatz then we could say

$$x_i := g f_i \tag{2.304}$$

where g is given by

$$g = a n c \tau \,. \tag{2.305}$$

This means that we have assumed the density of the particles along the line to be uniform. On the other hand if we assume that the particles are randomly and independently distributed with the value from equation (2.304) as a mean then we can set up for the distribution of the $x_i$ the Bernoulli expression

$$p(x_i) = \binom{f_i}{x_i} g^{x_i} (1-g)^{f_i - x_i} \,. \tag{2.306}$$

We have already that $N \gg gN \gg 1$ from equations (2.303) and (2.305) so that we may approximate to $p(x_i)$ by the gaussian distribution

$$p(x_i) = (2\pi g f_i)^{-\frac{1}{2}} \exp -(x_i - g f_i)^2 / 2 g f_i \,. \tag{2.307}$$

From equation (2.302) we find easily that the transition probability is given by

$$w(\Delta, \Delta') = \sum p(x_1) p(x_2) \tag{2.308}$$

where the summation extends over all values of $x_1$ and $x_2$ which satisfy the relation

$$\Delta' - \Delta = 2(x_2 - x_1) \,. \tag{2.309}$$

It is convenient to replace this sum by an integral with limits $+\infty$ and $-\infty$. This is possible because $p(x_i)$ is a bell-shaped function. Performing this integral and expressing the $f_i$ in terms of N and $\Delta$, we obtain as an approximation to the first power in $g$ the result

$$w(\Delta,\Delta') = (2\pi Ng)^{-\frac{1}{2}}\, e^{-g\Delta^2/2N - (\Delta'-\Delta)(\Delta'-\Delta+4g\Delta)/8gN}. \qquad (2.310)$$

$w(\Delta,\Delta')$ is thus normalized with respect to $\Delta'$. The average value of $\Delta'$ follows from the equation

$$\Delta'_{av} = \int \Delta' w(\Delta,\Delta')\, d\Delta' = (1-2g)\Delta \quad . \qquad (2.311)$$

Hence, by analogy with equation (2.110) we have for the average rate of change of $\Delta$ ;

$$(d\Delta/dt)_{av} = (\Delta'_{av} - \Delta)/\tau = -2g\Delta/\tau \quad , \qquad (2.312)$$

which is negative, and has the same value as would have prevailed if the Stosszahlansatz had been adhered to throughout. For equation (2.302) would then have read

$$d\Delta/dt = -2g(f_1 - f_2)/\tau = -2g\Delta/\tau \quad . \qquad (2.313)$$

Finally from equation (2.310) we obtain

$$w(\Delta,\Delta) = (2\pi Ng)^{-\frac{1}{2}} e^{-g\Delta^2/2N} \quad . \qquad (2.314)$$

Equations (2.310) and (2.106) give for large $\Delta$ the same expressions for $T(\Delta)$ and $\mathcal{H}(\Delta)$ that we had before for the urn model. The discussion at the end of the last section therefore still applies. Most of the results in this chapter have appeared in ter Haar and Green (1953). There is one other point which should be emphasized. This is that the procedure by which we divide the time coordinate into elements of length $\tau$ and then consider the events which take place in these intervals quite separately is not self explanatory. In the urn model

there was no doubt that the process actually went forward in this way, but for a mechanical model this might be in question. The same objection is likely to hold for all the succeeding models, so we defer the discussion of this point until the final chapters when there will be more material from which to draw conclusions.

## Chapter III

### §1. The Ehrenfests' Wind-Wood Model.

This model, which is also known as the 'wind-tree' model due to a fancied resemblance to the four winds blowing upon a plantation of conifers, was first introduced by the Ehrenfests (1911) in the review article which has been frequently mentioned already. Their purpose was to construct a simple mechanical model which should demonstrate the influence of the Stosszahlansatz upon the approach of a system to its equilibrium state. It is reasonable to suppose that they had also intended to investigate the effect in this model of the abandonment of the Stosszahlansatz, and to construct a $\Delta$-curve as they had already done in the case of the urn model. As far as we know this was not done, at least no such results were ever published, and for this reason this chapter will be devoted to an investigation along these lines. The treatment is similar to that of ter Haar and Green (1954).

The model that we consider here is not exactly the same as the original, but is a slight modification of it devised by ter Haar (1954, App. 1). We suppose the infinite plane to contain two types of particle. The first type which we will call Q-molecules (the 'woods')

are squares of semi-diagonal length a, and are distributed randomly over the plane with an average surface density of n per unit area. They are fixed in position in such a way that the diagonals are parallel, and we choose rectangular axes x and y parallel to these diagonals. (See figure 4). The density n and the length a are supposed to be such that a is much less than the average distance between the Q-molecules. For the second type, P-molecules, we have a large number N per unit area of point particles (the 'wind') which are free to move only in one of the four directions given by the axes +x, +y, -x and -y. We denote these four directions by the suffices 1,2,3 and 4 respectively. We assume that there are no interactions between the P-molecules themselves but that they may collide perfectly elastically with the Q-molecules, so that although their directions of motion may be changed yet they will still be one of the four just mentioned. Their absolute velocities will not be altered by collisions and we assume that these are all the same and equal to c.

We restrict ourselves to a unit area of the plane, which we assume to contain N P-molecules and n Q-molecules. This is a reasonable assumption so long as N is very large compared to unity, for then the fluctuations in the number of P-molecules in a unit area will be negligibly small as compared to N. In the

original Ehrenfests' model the total number of P-molecules was finite, but that of the Q-molecules was infinite, so that there was no need to consider such fluctuations. This advantage is offset in practice as we will show presently. On the above assumption then, we may denote the number of P-molecules moving in any of the four directions at a particular moment by the variables $f_1$, $f_2$, $f_3$ and $f_4$, and then the sum of these is constant;

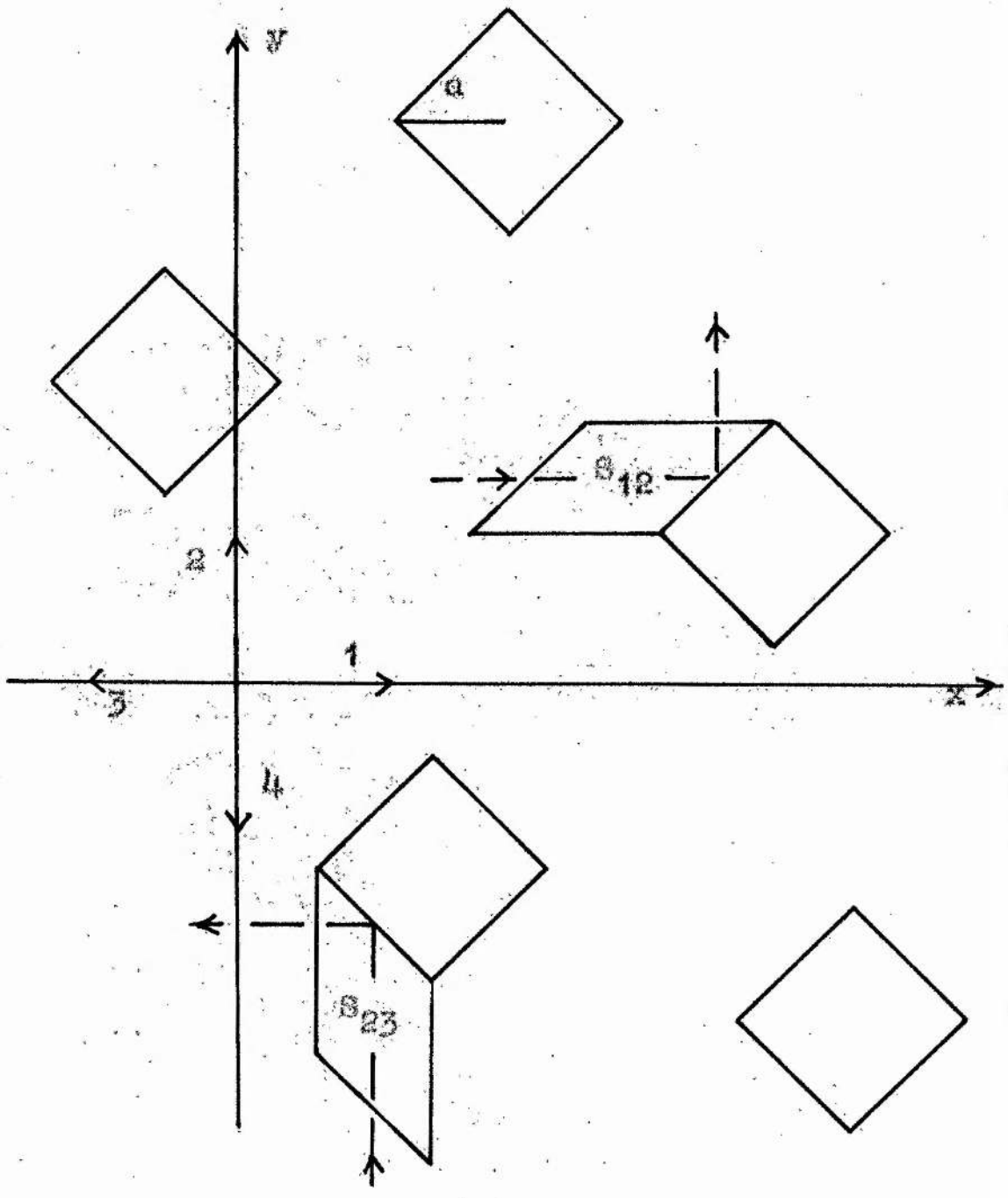
$$f_1+f_2+f_3+f_4 = N. \qquad (3.101)$$

The distribution is time dependent as are the variables $f_i$, so we consider the system again after the lapse of a time $\tau$. Let us suppose $\tau$ to be so short that the probability of a P-molecule making more than one collision during $\tau$ is very small indeed. In other words suppose that the distance travelled by a P-molecule in $\tau$ is much less than the mean free path, or

$$c\tau \ll 1/na \ . \qquad (3.102)$$

The change of the state of the system with time will be found by the consideration of the changes in the $f_i$ due to collisions. Let the number of P-molecules which change their motion from direction i to direction j due to collisions in a time $\tau$ be $x_{ij}$. This number is given by the equation

$$x_{ij} = n S_{ij} f_i \qquad (3.103)$$




The Wind-Wood Model.

Figure 4

where $S_{ij}$ is the area of a parallelogram of length c erected on the edge which is in the $-i,j$ quadrant of one of the squares. The $S_{ij}$ are all of the same area, so that defining the quantity g by

$$g = nc\tau a = n S_{ij} \quad , \tag{3.104}$$

we have for the differential equations of the change of $f_i$ with time the set of equations

$$\left.\begin{aligned} df_1/dt &= (f_2+f_4-2f_1)g/\tau \\ df_2/dt &= (f_3+f_1-2f_2)g/\tau \\ df_3/dt &= (f_4+f_2-2f_3)g/\tau \\ df_4/dt &= (f_1+f_3-2f_4)g/\tau \end{aligned}\right\} \quad . \tag{3.105}$$

By combining these differential equations in various ways we obtain the further set

$$\left.\begin{aligned} d(f_1-f_3)/dt &= (-2g/\tau)(f_1-f_3) \\ d(f_2-f_4)/dt &= (-2g/\tau)(f_2-f_4) \\ d[(f_1+f_3)-(f_2+f_4)]/dt &= (-4g/\tau)[(f_1+f_3)-(f_2+f_4)] \end{aligned}\right\} , \tag{3.106}$$

from which it follows immediately that as $t \to \infty$, then

$$f_1 \to f_3 \ , \ f_2 \to f_4 \text{ and } (f_1+f_3) \longrightarrow (f_2+f_4) \ ,$$

so that eventually

$$f_1^e = f_2^e = f_3^e = f_4^e = N/4 \quad , \tag{3.107}$$

by virtue of equation (3.101). The superscript e denotes the equilibrium state which is obviously given by the distribution described in equation (3.107). We have

thus shown that in this model any state will tend, as a result of elastic collisions, exponentially with increasing time to the equilibrium state. The disadvantage of the original Ehrenfest model is that the quantity $g/\tau$ which gives the rate of approach to equilibrium is then undetermined since the total number of Q-molecules is infinite in that model.

The method that has been used is basically the same as that employed to derive the Maxwell distribution law. Here, as there, an important assumption has been made in order to obtain equation (3.103). We have tacitly assumed that the number of molecules present in an area $S_{ij}$ is in the same ratio to $f_i$ as is the area $S_{ij}$ to the total area considered (in this case unity). This is the Stosszahlansatz for this system. It implies also the constancy of the density of P-molecules over the area $S_{ij}$. We introduce fluctuations by assuming instead that the number of particles in $S_{ij}$ is given by the random variable $x_{ij}$. Since the Stosszahlansatz is supposed to pick out the most probable numbers of collisions (see page 8) we take these variables $x_{ij}$ as being distributed randomly with the Stosszahlansatz values given by equation (3.103) as means, so that

$$(x_{ij})_{av} = g f_i \quad , \qquad (3.108)$$

where g is defined by equation (3.104). It is then very plausible to take the distributions of the $x_{ij}$ as being governed by the bernoullian law

$$p(x_{ij}) = \binom{f_i}{x_{ij}} (gf_i)^{x_{ij}} (1-gf_i)^{f_i - x_{ij}} , \qquad (3.109)$$

where $\binom{a}{b}$ is the binomial coefficient. With the assumption that

$$N \gg gN \gg 1 , \qquad (3.110)$$

we may approximate to this by the gaussian distribution

$$p(x_{ij}) = (2\pi gf_i)^{-\frac{1}{2}} e^{-(x_{ij}-gf_i)^2/2gf_i} . \qquad (3.111)$$

The assumption (3.110) is reasonable since by equations (3.102) and (3.104) g is defined as being of very small magnitude.

The differential equations (3.105) now become

$$\left.\begin{aligned} df_1/dt &= (x_{21}+x_{41}-x_{12}-x_{14})/\tau \\ df_2/dt &= (x_{12}+x_{32}-x_{21}-x_{23})/\tau \\ df_3/dt &= (x_{43}+x_{23}-x_{34}-x_{32})/\tau \\ df_4/dt &= (x_{34}+x_{14}-x_{43}-x_{41})/\tau \end{aligned}\right\} . \qquad (3.112)$$

The equilibrium values given by equation (3.107) still hold, however the approach of the $f_i$ to the $f_i^e$ will no longer be described by monotonic exponential curves but by stochastic tracks, since the $x_{ij}$ are stochastic variables. The $f_i$ are always discrete variables, but if N is sufficiently large they may be practically regarded

as continuous.

In order to obtain the Ehrenfests' $\Delta$-curve as we did in the last chapter for the one dimensional variant of this model we define a variable $\Delta$ as describing the departure of the system from its equilibrium state by

$$\Delta = \sum_{i=1}^{4}(f_i - f_i^e)^2/2f_i^e$$
$$= \frac{2}{N}\sum_{i=1}^{4}(f_i - \frac{N}{4})^2 \quad , \qquad (3.113)$$

since $f_i^e = N/4$ . At equilibrium and nowhere else, $\Delta$ will equal zero, and it will be positive at all other times. It will be a discrete variable just as are the $f_i$. The variation of $\Delta$ with time is readily derived from equation (3.113):

$$d\Delta/dt = \frac{4}{N}\sum_{i=1}^{4} f_i df_i/dt \quad , \qquad (3.114)$$

since $\sum_{i=1}^{4} df_i = 0$. Using the Stosszahlansatz expressions for $df_i/dt$ from equations (3.105) we obtain

$$d\Delta/dt = \frac{-8g}{N\tau}\left[\sum_{i=1}^{4} f_i^2 - (f_1f_2 + f_2f_3 + f_3f_4 + f_4f_1)\right] . \qquad (3.115)$$

Since there is not here a one-one correspondence between $\Delta$ and the state defined by $(f_1, f_2, f_3, f_4)$ we must take an average of some sort. We will discuss this question more thoroughly in Chapter V when we can compare the results from all the models, but we just mention here that the average of $f_if_{i+1}$ may be taken as equal to $N^2/16$ so that from equations (3.101), (3.113) and (3.115) it follows that the average value of the rate of change of $\Delta$ under

the Stosszahlansatz is given by the equation

$$[d\Delta/dt]_{av} = -4g\Delta/\tau \quad . \qquad (3.116)$$

§2. The Markoff-Chandrasekhar Method.

In order to determine the behaviour of the $\Delta$-curve which is formed by the model it is necessary to calculate the probability distribution and the transition probability of the variable $\Delta$. It was found that since $\Delta$ had the form of the sum of a set of stochastic variables that a method invented by Markoff (1912) and developed later by Chandrasekhar (1943, Ch. I, § 2) for use in random walk problems was particularly convenient. This method has the considerable advantage that the integrals involved are readily calculated by means of the calculus of the complex variable, while in the more direct approach the integrals are most unwieldy because of the irregularity of the domains of integration. In fact the case with two variables evaluated in Chapter II represents the limit of convenience. The procedure is now standard practice in statistics, involving as it does the preliminary calculation of the Fourier transform of the required probabilities (see, for example, Cramér, 1945).

Suppose that we require the probability $w(\Phi_o)d\Phi_o$ that the variable $\Phi$ satisfies the condition

$$\Phi_o - \tfrac{1}{2}d\Phi_o \leq \Phi \leq \Phi_o + \tfrac{1}{2}d\Phi_o \quad . \qquad (3.201)$$

Further, let $\Phi$ be the sum of functions $\phi_i$ ,

$$\Phi = \sum_{i=1}^{s} \phi_i \quad , \tag{3.202}$$

where the $\phi_i$ are functions of the set of k stochastic variables $q_1, q_2, \ldots, q_k$ so that

$$\phi_i = \phi_i(q_1, \ldots, q_k) \quad . \tag{3.203}$$

Suppose that we are given the simultaneous probability

$$\omega(q_1, \ldots, q_k) dq_1 dq_2 \ldots dq_k \equiv \omega(\underline{q}) d\underline{q} \tag{3.204}$$

that the variables $q_1, \ldots, q_k$ lie in the ranges $q_1$ to $q_1+dq_1, \ldots, q_k$ to $q_k+dq_k$ respectively. The equivalent expression is a shorthand notation. The required probability $w(\Phi_o)d\Phi_o$ is evidently given by

$$w(\Phi_o)d\Phi_o = \int \cdots \int \omega(q_1, \ldots, q_k) dq_1 \ldots dq_k \tag{3.205}$$

where the integrals are taken over only those parts of k-dimensional space in which the inequalities (3.201) are satisfied. To circumvent the difficulty of evaluating this integral we introduce a factor $\pi(q_1, \ldots, q_k)$ such that

$$\left.\begin{aligned} \pi(q_1, \ldots, q_k) &= 1 \quad \text{if} \quad \Phi_o - \tfrac{1}{2}\alpha\Phi_o \leq \Phi \leq \Phi_o + \tfrac{1}{2}\alpha\Phi_o \\ &= 0 \quad \text{otherwise.} \end{aligned}\right\} \tag{3.206}$$

Then

$$w(\Phi_o)d\Phi_o = \int \cdots \int \omega(q_1, \ldots, q_k)\pi(q_1, \ldots, q_k) dq_1 \ldots dq_k \quad , \tag{3.207}$$

where now the integration extends over all q-space. The function $\pi(\underline{q})$ may be expressed explicitly.

Consider the Dirichlet integral $\delta$ , where

$$\delta = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{\sin(a\rho)}{\rho}\, e^{i\gamma\rho}\, d\rho \quad . \tag{3.208}$$

This has the property that

$$\left.\begin{aligned} \delta &= 1 \quad \text{whenever} \quad -a < \gamma < +a \\ &= 0 \quad \text{otherwise.} \end{aligned}\right\} \tag{3.209}$$

If we now let

$$a = \tfrac{1}{2}d\Phi_0 \quad \text{and} \quad \gamma = \sum_{i=1}^{s}\phi_i - \Phi_0 \quad , \tag{3.210}$$

then it can be seen that $\delta$ satisfies the conditions (3.206) for the function $\pi(q_1,..,q_k)$.

Substituting now for $\pi$ from equation (3.208) into (3.207) we obtain

$$\begin{aligned} w(\Phi_0)d\Phi_0 &= \frac{1}{\pi}\int_\rho\int\cdots\int q^{\omega(\underline{q})}\, \frac{\sin(\frac{1}{2}d\Phi_0\rho)}{\rho} e^{i\rho\sum_{i=1}^{s}\phi_i - \rho\Phi_0}\, d\underline{q}\, d\rho \\ &= \frac{d\Phi_0}{2\pi}\int_{-\infty}^{+\infty} e^{-i\rho\Phi_0} A(\rho)\, d\rho \quad , \end{aligned} \tag{3.211}$$

where $A(\rho)$ is given by the equation

$$A(\rho) = \int\cdots\int e^{i\rho\sum_{i=1}^{s}\phi_i}\, \omega(q_1,\ldots,q_k)\, dq_1..dq_k \quad . \tag{3.212}$$

This method enables us to calculate the probability of $\Delta$ for all the models that we will consider. For the transition probability a slight modification is necessary.

Let $\Phi$ be defined as before, and let the variation $\delta\Phi$ be given by the sum

$$\delta\Phi = \sum_{j=1}^{t}\delta\phi_j \quad , \tag{3.213}$$

where

$$\delta\phi_j = \delta\phi_j(q_1,\ldots,q_k;r_1,\ldots,r_l) \qquad (3.214)$$

and $r_1,\ldots,r_l$ are another set of stochastic variables. The probability of $r_n$ lying within the limits $r_n$ and $r_n+dr_n$ is denoted by $\omega_n(r_n)dr_n$, where $n=1,2\ldots l$.

Thus the double probability that $\Phi$ should satisfy the inequality (3.201) and that at the same time $\delta\Phi$ should fulfil the similar one

$$\delta\Phi_0 - \tfrac{1}{2}d(\delta\Phi_0) \leqslant \delta\Phi \leqslant \delta\Phi_0 + \tfrac{1}{2}d(\delta\Phi_0) \qquad (3.215)$$

is expressed by the equation

$$w(\Phi_0)w(\delta\Phi_0)d\Phi_0 d(\delta\Phi_0) = \int\cdots\int \omega(\underline{q})\prod_{n=1}^{l}\omega_n(r_n)d\underline{q}\prod_{n=1}^{l}dr_n. \qquad (3.216)$$

By introducing a second factor $\pi'$ of the same type as the first we have

$$w(\Phi_0)w(\delta\Phi_0)d\Phi_0 d(\delta\Phi_0) = \int\cdots\int \pi(\underline{q})\pi'(\underline{q};r_1,\ldots,r_l)\prod_{n=1}^{l}\omega_n(r_n)\omega(\underline{q})d\underline{q}\prod_{n=1}^{l}dr_n \qquad (3.217)$$

the integration here being over all of kl-dimensional space and not just over those parts of it where inequalities (3.201) and (3.215) are true. Using expressions similar to (3.208) and (3.210) to define $\pi'$ and then substituting in the above equation we obtain

$$w(\Phi_0)w(\delta\Phi_0)d\Phi_0 d(\delta\Phi_0) = \frac{d\Phi_0 d(\delta\Phi_0)}{4\pi^2}\int_{-\infty}^{+\infty}\int e^{-i\rho\Phi_0}\Lambda(\rho,\sigma)e^{-i\sigma\delta\Phi_0}d\rho d\sigma, \qquad (3.218)$$

where $\Lambda(\rho,\sigma)$ is defined by

$$\Lambda(\rho,\sigma) = \int\cdots\int e^{i\rho\sum_{i=1}^{s}\phi_i}\, e^{i\sigma\sum_{j=1}^{k}\delta\phi_j}\,\omega(\underline{q})\prod_{n=1}^{l}\omega_n(r_n)\,d\underline{q}\prod_{n=1}^{l}dr_n. \qquad (3.219)$$

The functions $\Lambda(\rho)$ and $\Lambda(\rho,\sigma)$ are the Fourier

transforms of the probabilities. A useful result is that if $w(\Phi)$ is to be normalized then $\Lambda(0) = 1$, and similarly for $\Lambda(\varsigma,\sigma)$. It is necessary to derive the double probability $w(\Phi_o)w(\delta\Phi_o)$ because both $\phi_i$ and $\delta\phi_j$ are functions of the same variables $\underline{q}$ so that $\delta\phi_j$ depends upon $\phi_1$. The transition probability follows simply by division of the product.

## §3. Derivation of the Formulae.

We have by now obtained nearly all the quantities which are required to derive the formulae in which we are interested. An exception is the compound probability of the set of variables $f_1, f_2, f_3$ and $f_4$. Since the sum of these is constant and equal to N, they are dependent. We denote the probability by $p(f_1,f_2,f_3,f_4)$. The P-molecules were assumed to be distributed randomly over the plane so there is an equal likelihood of any one of them moving in any of the four possible directions. The probability is therefore represented by the bernoullian distribution

$$p(f_1,f_2,f_3,f_4) = \frac{N!}{f_1!f_2!f_3!f_4!}\left(\frac{1}{4}\right)^N \qquad (3.301)$$

Taking logarithms of both sides and using Stirling's formula for the factorials,

$$\ln f! = (f+\tfrac{1}{2})\ln f - f + \tfrac{1}{2}\ln(2\pi) \quad , \qquad (3.302)$$

we have

$$\ln p(f_1,..,f_4) = -N\ln 4 + (N+\tfrac{1}{2})\ln N - \frac{3}{2}\ln 2\pi - \sum_{i=1}^{4}(f_i+\tfrac{1}{2})\ln f_i \qquad (3.303)$$

Under the assumption that the values of $f_i$ are not greatly different from the most probable value $N/4$ we have been able to take the $f_i$ to be large as compared to unity in order to use the formula (3.302). This is justified since $p(f_1,..,f_4)$ falls off sharply from its maximum. Even though very large values of $\Delta$ are thus excluded the restriction is not serious since we are interested mainly in fluctuations about the equilibrium value $\Delta=0$. Defining the new set of variables by the equation

$$a_i = f_i - N/4 \quad , \tag{3.304}$$

we may now take $4a_i/N \ll 1$. Introducing these $a_i$ into equation (3.303) instead of the $f_i$ and expanding the logarithms in series, neglecting powers higher than the second in $4a_i/N$, we eventually obtain

$$\begin{aligned} p(a_1,..,a_4) \text{ or } p(f_1,..,f_4) &= 16(2\pi N)^{-3/2} e^{-(2/N)\sum_{i=1}^{4} a_i^2} \\ &= 16(2\pi N)^{-3/2}\ e^{-\Delta} \quad . \end{aligned} \tag{3.305}$$

In order to calculate $w(\Delta)$ we now utilize the expressions obtained in the previous section. We have instead of equations (3.202) to (3.204)

$$\phi_i = 2a_i/N \ ; \quad \Delta = \sum_{i=1}^{4} \phi_i \ ; \ \omega(q_1,..,q_k)=p(a_1,..,a_4) \ . \tag{3.306}$$

The variables $q_i$ are replaced by the $a_i$. However, these last are dependent, in fact $\sum_i a_i = 0$, so that we replace

$\alpha_4$ by $-(\alpha_1+\alpha_2+\alpha_3)$ thus obtaining as the counterpart of equation (3.212)

$$A(\rho)=\int_{-\infty}^{+\infty}\int\int 16(2\pi N)^{-3/2} e^{-\frac{4}{N}(1-i\rho)\left[\sum_{i=1}^{3}\alpha_i^2+\sum_{i<j}\alpha_i\alpha_j\right]} d\alpha_1 d\alpha_2 d\alpha_3 . \qquad (3.307)$$

The lower limits of the integrations should strictly speaking be $-N/4$ but for the reasons aforesaid they may be taken as $-\infty$. Integrating over the $\alpha_i$ we get

$$A(\rho) = (1-i\rho)^{-3/2} . \qquad (3.308)$$

Analogously to equation (3.211) the probability distribution of $\Delta$ is then given by

$$w(\Delta)d\Delta = \frac{d\Delta}{2\pi}\int_{-\infty}^{+\infty}(1-i\rho)^{-3/2} e^{-i\rho\Delta} d\rho \qquad (3.309)$$

which may be evaluated by means of contour integration as is described in the Appendix, section 2. The final result is

$$w(\Delta) = 2(\Delta/\pi)^{\frac{1}{2}} e^{-\Delta} , \qquad (3.310)$$

which is normalized, as we would expect since $A(0) = 1$.

The transition probability that $\Delta$ should change to $\Delta'$ in the time $\tau$ is derived in a similar manner. Firstly we define the variable $\delta\Delta = \Delta - \Delta'$ by the variation of equation (3.113) as

$$\delta\Delta = \frac{4}{N}\sum_{i=1}^{4}(f_i - N/4)\,\delta f_i$$

where the $\delta f_i$ are given by the differential equations (3.112) in terms of the $x_{ij}$. Since $\sum_{i=1}^{4}\delta f_i = 0$, we have

$$\delta\Delta = (4/N)\sum_{i=1}^{4} f_i\,\delta f_i . \qquad (3.311)$$

The $x_{ij}$ can now be taken as the stochastic variables $r_n$ of equation (3.214) so that we may write by analogy:

$$\delta\Delta = \sum_{j=1}^{t} \delta\phi_j \quad [3.213] : \quad \delta\phi_j = \frac{4}{N} f_j \delta f_j \quad [3.214]$$

The probabilities $p(x_{ij})$ replace the $\omega_n(r_n)$ defined in section 2, and so the bivariate transform is given by

$$A(\rho,\sigma) = \int\cdots\int p(f_1,..,f_4) \prod_{j=i+1} p(x_{ij})\, e^{\frac{4}{N} i\rho \sum_j f_j \delta f_j + \frac{2i\sigma}{N} \sum_i (f_i - \frac{1}{4}N)^2} df_1 df_2 .. dx_{12} .. dx_{41} \quad . \quad (3.312)$$

Substituting the values already obtained for $p(f_1,..,f_4)$, $p(x_{ij})$ and $\delta f_i$ from equations (3.305),(3.111) and (3.112) and integrating over the eight variables $x_{ij}$ from $+\infty$ to $-\infty$, the result can be expressed as

$$A(\rho,\sigma) = 16(2\pi N^3)^{-\frac{1}{2}} \int_0^{\infty}\int_0^{\infty}\int_0^{\infty} e^{-\frac{1}{N}E}\, df_1 df_2 df_3 \quad , \quad (3.313)$$

where

$$E = g\rho i[(f_1-f_4)^2+(f_4-f_3)^2+(f_3-f_2)^2+(f_2-f_1)^2] + \frac{2f\rho^2}{N}(f_1+f_4)(f_1-f_4)^2+(f_4+f_3)(f_4-f_3)^2+(f_3+f_2)(f_3-f_2)^2 + (f_2+f_1)(f_2-f_1)^2 + (1-\frac{2i\sigma}{N}) \sum_{i=1}^{4} (f_i - \frac{N}{4})^2 \quad .$$

It is convenient at this stage to reintroduce the variables $a_i$ given by equation (3.304), and remembering that $a_4 = -(a_1+a_2+a_3)$, E may be rewritten in the form

$$E = a_1^2(3A+C) + a_2^2(2A+C) + a_3^2(3A+C) + a_1a_2(2A+C) + a_2a_3(2A+C) + a_3a_1(4A+C) \quad (3.314)$$

where

$$A = 2(g\varsigma i + \varsigma^2 g) \quad \text{and} \quad C = 1 - i\sigma \quad . \tag{3.315}$$

In deriving equation (3.314) we have neglected such terms as $a_1^2 a_2$ since $a_1^2 a_2 \ll a_1^2 N$ according to our previous assumptions. The expression for $A(\varsigma,\sigma)$ is now obtained by performing the integration

$$A(\varsigma,\sigma) = 16(2\pi N^3)^{-\frac{1}{2}} \int\int\int_{-\infty}^{+\infty} e^{-\frac{4.E}{N}} \, da_1 da_2 da_3 \quad ,$$

with the result that

$$A(\varsigma,\sigma) = (4A+C)^{-\frac{1}{2}}(2A+C)^{-1} \quad . \tag{3.316}$$

By analogy with equation (3.218) we have the equation

$$w(\Delta)w(\delta\Delta) = \frac{1}{4\pi^2} \int\int_{-\infty}^{+\infty} e^{-i\sigma\Delta - i\varsigma\delta\Delta} A(\varsigma,\sigma) \, d\varsigma \, d\sigma \quad . \tag{3.317}$$

If we consider first of all the integration over and let I denote the integral

$$I = \int_{-\infty}^{+\infty} (4A - i\sigma + 1)^{-\frac{1}{2}} (2A - i\sigma + 1) \, e^{-i\sigma\Delta} \, d\sigma \quad , \tag{3.318}$$

then I may be evaluated by contour integration. Since the procedure is rather lengthy it is given in the Appendix, section 3, and the value obtained is given by

$$I = \pi(2/A)^{\frac{1}{2}} \, \mathrm{erf}[(2A\Delta)^{\frac{1}{2}}] \, e^{-2\Delta(A+\frac{1}{2})} \quad . \tag{3.319}$$

The expression erf(x) denotes the error function. Equation (3.317) has now been reduced to

$$w(\Delta)w(\delta\Delta) =$$

$$\frac{1}{4\pi^2} \int_{-\infty}^{+\infty} (2\varsigma i + \varsigma^2 g)^{-1/2} \, \mathrm{erf}\left[2\Delta g(\varsigma i + \varsigma^2 g)\right]^{\frac{1}{2}} e^{-i\varsigma\delta\Delta - 2\Delta(A+\frac{1}{2})} \, d\varsigma \quad . \tag{3.320}$$

where the value of $\Lambda$ given by (3.315) has been introduced. This integral is evaluated approximately by the method described in the Appendix, § 3, using the fact that $\mathrm{erf}(x) \simeq x$ when $x \ll 1$. We thus obtain

$$w(\Delta)w(\delta\Delta) = (4\pi^2 g)^{-\frac{1}{2}} e^{-\Delta - (\delta\Delta + 4g\Delta)^2/16g\Delta} . \qquad (3.321)$$

Dividing through by the function $w(\Delta)$ expressed in equation (3.310) we find for the transition probability

$$w(\Delta, \Delta') = (16\pi g\Delta)^{-\frac{1}{2}} e^{-(\Delta' - \Delta + 4g\Delta)^2/16g\Delta} . \qquad (3.322)$$

This expression is normalised with respect to $\Delta'$, while the average value of $\Delta'$ is given by

$$\Delta'_{av} = \int \Delta' w(\Delta, \Delta') d\Delta' = (1-4g)\Delta . \qquad (3.323)$$

The average rate of change of $\Delta$ is then calculated in the same way as for the one dimensional model, giving a similar result;

$$(d\Delta/dt)_{av} = (\Delta'_{av} - \Delta)/\tau = -4g\Delta/\tau . \qquad (3.324)$$

We may compare this result with the expression (3.116) obtained when the Stosszahlansatz was still in force. It should be noted that the averages are of different sorts, as is indicated by the use of round and square brackets. The recurrence probability is obtained from equation (3.322) by putting $\Delta'$ equal to $\Delta$. Thus

$$w(\Delta, \Delta) = (16\pi g\Delta)^{-\frac{1}{2}} e^{-g\Delta} . \qquad (3.325)$$

The mean life time and the average time of recurrence

may now be expressed in terms of $\Delta$ and $g$ by introducing the values of $w(\Delta)$ and $w(\Delta,\Delta)$ of equations (3.310) and (3.325) into the formulae for $T(\Delta)$ and $\Theta(\Delta)$ given by (2.203) and (2.210). Having done this we are left with

$$T(\Delta) = \tau\left[1-(16\pi g\Delta)^{-\frac{1}{2}}e^{-g\Delta}\right]^{-1} \qquad (3.326)$$

and

$$\Theta(\Delta) = T(\Delta)\left[\tfrac{1}{2}(\pi/\Delta)^{\frac{1}{2}}\, e^{\Delta} -1\right] \quad . \qquad (3.327)$$

As in the previous cases we see that $T(\Delta)$ is very nearly equal to $\tau$, and is almost independent of $\Delta$, while $\Theta(\Delta)$ is practically equal to $\tau/w(\Delta)$. Although the results for this model appear slightly different from those for the one dimensional case due to the absence of the constant N, this is merely caused by the definition of $\Delta$ having been made in such a way that N is implicit in $\Delta$. This will be found to be the most satisfactory mode of definition when we come to discuss more general models in the next chapter, and we deliberately chose the other definition in the previous case in order to emphasise the similarity to the urn model.

## Chapter IV

### §1. The Generalized Class of Model.

Up to now the only mechanical model that we were concerned with was the wind-wood model. Regarded physically this model has obviously little connection with reality, and it is desirable to extend the range of investigation to include if possible the whole variety of models which fall into the class described in Chapter I. This has been attempted by Green and ter Haar (1954). The artificiality of the wind-wood model does not detract from its usefulness as a guide to the techniques to be employed for all the models in this category. The opposite is true, for since the simpler model is less complicated physically, the predominantly mathematical techniques show the more clearly. The class of model under investigation includes all those where there are present two types of particle, which we will name type P and type Q to retain the nomenclature of the previous chapter. Those particles of type Q are supposed to be fixed in space in some random configuration, while those of type P are free to move amongst them and to interact with them in some determined manner. The way in which the interaction takes place may be given by the geometrical properties of the particles as in the wind-wood model, or else by an assigned law.

It will be demonstrated in this chapter that within certain restrictions the nature of this law is irrelevant to the form of the final results.

The moving type P particles are assumed to be such that interactions of the kind P-P may be neglected. The average densities per unit volume of the P and Q particles are given by the large numbers N and n respectively. By assuming N and n to be very large as compared to unity we may neglect the possible fluctuations in the numbers of P and Q particles in the unit volume which we take as containing the system. End effects which might occur at the boundaries of the unit volume are neglected throughout. In addition to the situation of the system in coordinate space we must also recognize that for the general case the state of a particle will be described by a point in phase space. In accordance with the basic principles of statistical mechanics formulated in chapter I this phase space is to be divided up into elementary cells. Let there be $2m+1$ of these, each of volume $\delta\omega$. We will label each cell by means of the indices $\nu$, where $\nu = -m,\ldots,-1,0,+1,\ldots,+m$. The choice of m, and $\delta\omega$, is determined by the two opposing conditions that firstly each cell should contain on average the representative points of very many particles, and that secondly the cells should be so small as to be experimentally indistinguishable The whole system is taken to be isolated, and the total

phase space available to it is denoted by $\Omega$. Thus

$$\delta\omega = \Omega/(2m+1) \ . \qquad (4.101)$$

Generally speaking $2m+1$ may be treated as being a large number if N is large. Finally the mechanism of interaction between the two types of particle must be given. Suppose the probabilityvthat a particle which was initially in a cell denoted by the index v should be transferred as a result of a single interaction to the cell v' is denoted by $p(v,v')$. The cross-section of the collisions of the P particles with those of the type Q is given by the quantity $\sigma$, which completes the definition of the model.

Since we will be concerned with the change of the system with time we must now study the structure of the time scale. As before, in order to deal with collision processes it is most convenient to divide the time scale into elements of constant duration, say $\tau$. We choose $\tau$ to be so short that there is a negligible probability of any one particle undergoing more than one collision during this time. Therefore the distance travelled by the particle during $\tau$ must be much less than the mean free path, or

$$c\tau \ll 1/n\sigma \ , \qquad (4.102)$$

if the absolute velocities are constant and equal to c. If they are not constant, but have a maximum value V say,

we then assume that

$$\tau \ll 1/n\sigma V \quad . \tag{4.103}$$

The probability that a particle makes a collision during $\tau$ is then given by $g_v$ where

$$g_v = n\sigma\tau c_v \quad , \tag{4.104}$$

where we are dealing with a particle in the vth cell and $c_v$ is to be understood as the velocity of such a particle. From the definition it can be seen that $g_v \ll 1$. Equation (4.104) has been derived in accordance with the Stosszahlansatz. As we will show in the next chapter once this assumption has been made then the system will be found to approach the equilibrium situation exponentially as $t \to \infty$.

The occupation numbers of the $2m+1$ cells which give the numbers of P particles which have representative points lying in the cells v at the time t we denote by $f_v(t)$ or simply $f_v$. Since the total number of P particles is assumed to be constant there is the relation

$$\sum_v f_v = N \quad , \tag{4.105}$$

where here, as elsewhere, the symbol $\sum_v$ indicates summation over all $v = -m,..,-1,0,+1,..,+m$. The state of the system is characterized by the set of variables $f_v$ at any one time, and we will denote this set either by $\{f_v\}$ or else by Z (after the Ehrenfests' notation:

'Zustandsverteilung').

The differential equations for the variation of $\{f_v\}$ now follow by consideration of the number of particles which are transferred into the various cells at each collision. The result is

$$df_v/dt = (1/\tau) \sum_{v'} [g_{v'} p(v',v) f_{v'} - g_v p(v,v') f_v] \quad . \qquad (4.106)$$

The equilibrium situation is the stationary state attained when $df_v/dt = 0$;

$$df_v^e/dt = 0 = (1/\tau) \sum_{v'} (a_{v'v} f_{v'}^e - a_{vv'} f_v^e) \quad , \qquad (4.107)$$

where the superscript e denotes the equilibrium value, and we have introduced the quantity $a_{vv'}$ by means of the equation

$$a_{vv'} = g_v p(v,v') \quad . \qquad (4.108)$$

One solution of equation (4.107) is that for all v'

$$a_{v'v} f_{v'}^e = a_{vv'} f_v^e \quad . \qquad (4.109)$$

Since $a_{vv'}$ is the probability that a particle be transferred from cell v to cell v' in the time $\tau$, this solution also satisfies the principle of detailed balancing (Fowler, 1929), and therefore we take it as the only practicable solution. It should be noted that the quantity $a_{vv'}$ contains all the information relating to the mechanism of the collision processes, and thus that the form of $a_{vv'}$ is characteristic of the model.

In order to take account of the fluctuations which

arise when the Stosszahlansatz is abandoned we introduce the set of stochastic variables $x_{vv'}$, which we take to be the actual numbers of particles passing from cells v to v' in time $\tau$. The mean values of the $x_{vv'}$, are then given by those values which were obtained under the Stosszahlansatz. In this way

$$(x_{vv'})_{av} = a_{vv'}f_v \quad . \tag{4.110}$$

Under these conditions the differential equations (4.106) take on the form

$$df_v/dt = (1/\tau)\sum_{v'}(x_{v'v}-x_{vv'}) \quad . \tag{4.111}$$

§2. The Various Models.

By examining the mechanical properties of the particular models of the class under discussion it is possible to obtain expressions for the quantities $a_{vv'}$, and also, using equation (4.109), for the equilibrium distributions $\{f_v^o\}$. Therefore we will investigate the details of some classical models, and we will show that these fall into three main groups differentiated by the form of $a_{vv'}$. These groups contain the models in which $a_{vv'}$ is constant, is symmetric with respect to v and v', or depends only upon v'. In the first two categories equation (4.109) gives the result that $f_v^o$ will be constant, and this is especially important when we come to define

the function $\Delta$ .

We treat first of all the models in which $a_{vv'}$ is a constant. The most notable example of these is the Lorentz (1909) model of the conduction electrons in a metal. It is well known (compare, for example, ter Haar 1954, chap.X) that this model can account to a first approximation for the transport properties of a metal. Here the Q-particles are the fixed lattice points or metallic ions and the P-particles are the conduction electrons. We assume that the lattice-electron interactions are elastic and isotropic, and that electron-electron collisions may be neglected. Thus the absolute magnitude of the velocity of an electron does not change at a collision, and we need only consider electrons moving at one velocity, say c. This is equivalent to supposing that thermal equilibrium has been set up in the metal so that the velocity distribution is constant. Due to the isotropy of the collisions

$$p(v,v') = \text{constant} = 1/(2m+1)^2 \ , \qquad (4.201)$$

for normalization. The cells in phase space are set up by dividing the total solid angle $4\pi$ into 2m+1 equal elements each of solid angle $\delta\omega = 4\pi/(2m+1)$. Since $g_v$ is constant and defined by equation (4.104) the value of $a_{vv'}$ is also constant and is given by

$$a_{vv'} = g_v p(v,v') = nc\sigma\tau/(2m+1)^2 \ . \qquad (4.202)$$

Further, since by the definition of $\tau$ , $g_v \ll 1$, and since m is a large number, evidently $a_{vv'} \ll 1$.

By regarding the Q-particles as hard elastic spheres we can develop this model into one in which the collisions are no longer isotropic. In order to draw an analogy with the wind-wood model we consider now the two dimensional case where the Q-particles are discs of radius a, and the P-particles as before collide elastically. Again we may take the velocities as constant and equal to c. In this form the model has a similarity to the gas model of Rayleigh (1891). The division of phase space is performed by dividing the plane angle $2\pi$ into $2m+1$ cells, each defining a direction of the velocity vector. The 'volume' of each is now $\delta\omega = 2\pi/(2m+1)$. Elementary geometric reasoning gives the value of the transition probability as

$$p(v,v') = \cos[(v-v')\tfrac{1}{2}\delta\omega]\,\delta\omega/4 \quad . \qquad (4.203)$$

Again $g_v$ is constant and small so that the product of $g_v$ and $p(v,v')$ is both small and is symmetric with respect to interchange of v and v'. This ensures the constancy of $f_v^e$, as is shown by equation (4.109). This model may also be regarded as a generalization of the wind-wood model where the polygonal Q-molecules have now been transformed into discs. However in this case $p(v,v')$

has the irregular, but still symmetric form

$$\left.\begin{aligned} p(v,v') &= 0 \quad \text{if } v' \neq v \pm 1 \\ &= 1/8 \text{ otherwise.} \end{aligned}\right\} \tag{4.204}$$

By putting $m = 3/2$ the model may also be included in the general pattern. The irregularity accounts for the comparative difficulty of some of the calculations undertaken in the treatment of the wind-wood model.

Finally we consider two models in which the velocity is not constant. We take for simplicity one dimensional cases, so that only the velocity (or rather momentum) coordinates of phase space need be regarded. Let the Q-particles be some sort of radiating screens or lattice points in a metal. Let the maximum speed of a P-particle be V, and take the velocities in the +x-direction to be positive. We then divide the velocity range +V to -V into $2m+1$ cells each of extension $\delta\omega = 2V/(2m+1)$. In the first model we assume that the interactions are of such a type that

$$\left.\begin{aligned} p(v,v') &= \beta/|v| \qquad \text{if } v \neq v', \\ &= 1 - 2m\beta/|v| \quad \text{if } v = v', \end{aligned}\right\} \tag{4.205}$$

where $\beta$ is a constant. Physically this could mean that the electrons have a certain probability of adhering to the lattice points and that they are then emitted with random velocities. Equation (4.103) now gives the magnitude of $\tau$, and so $g_v = n\sigma v\tau$, where we have

written v for $c_v$. Thus

$$a_{vv'} = n\sigma\beta\tau \quad , \tag{4.206}$$

which is again constant. The $f_v^e$ are also constant.

In the second case we have the same type of model, but this time the transition probability is supposed to have the form

$$\left.\begin{aligned} p(v,v') &= \frac{\alpha}{|v|} e^{-\beta v'^2} \qquad \text{if } v \neq 0, \\ p(0,v') &= 0 \quad , \end{aligned}\right\} \tag{4.207}$$

where $\alpha$ and $\beta$ are constants. In this model the electrons adhere to the lattice points in the same way, but they are now emitted in such a manner as to correspond to a process of evaporation, so that the constant $\beta$ can be considered as proportional to $1/kT$. Again $g_v$ is dependent upon v, but $a_{vv'}$ is given by

$$a_{vv'} = n\sigma\tau\alpha\, e^{-\beta v'^2} \quad , \tag{4.208}$$

which is neither constant nor symmetric but depends only upon v'. The detailed balancing formula then shows that the equilibrium distribution is maxwellian, for

$$f_v^e = C\, e^{-\beta v^2} \quad , \tag{4.209}$$

where C and $\beta$ are constants.

By combining two of these models it is possible to produce one in which the whole of phase space is brought into play, for example a Lorentz model with a velocity distribution. To do this it is necessary merely to

increase the number of phase cells, and this does not affect the basic procedure in any way. In order to reduce the complications of notation we will leave the models in their simplest forms.

§3. The Definition of $\Delta$.

In order to define the function $\Delta$ which is to give a measure of the deviation of the system from its equilibrium situation the obvious course is to start from the quantity H which due to the H-theorem has the same property. We write

$$H = H_{min} + \Delta \quad , \tag{4.301}$$

where $H_{min}$ is the stationary value of H at equilibrium, and $\Delta$ is a positive function, zero at equilibrium and nowhere else. We now show how an expression for $\Delta$ may be found in terms of the sets of occupation numbers $\{f_v\}$ and $\{f_v^e\}$.

From equation (1.403) we have that

$$H(Z) = -\ln W(Z) + \text{constant} \quad , \tag{4.302}$$

where Z denotes the situation described by the set $\{f_v\}$ and W(Z) is the volume of the Z-star belonging to this situation. From the definition of the Z-star given in Chapter I we see that the probability p(Z) or $p\{f_v\}$ of the situation Z is intimately related to W(Z). For,

assuming that the cells in phase space have equal volumes $\delta\omega$, and that the a priori probabilities of a particle being in any cell are equal and proportional to the volumes, then $p(Z)$ is given by the conditional probability of the set $\{f_\nu\}$ under the restriction that the sum of the $f_\nu$ is constant and equal to N. Thus

$$p(Z) = C.N! \prod_\nu \frac{(\delta\omega)^{f_\nu}}{f_\nu!} \quad . \tag{4.303}$$

C is a constant of normalization. Apart from this constant factor $p(Z)$ is identical with $W(Z)$ as defined by equation (1.402). Thus equation (4.302) may be rewritten as

$$H(Z) = -\ln p(Z) + \text{constant} \quad . \tag{4.304}$$

If the $f_\nu$ are large numbers as they must be on the average to conform with the conditions stated in section 1, then we may employ Stirling's formula to evaluate the factorials approximately. Taking logarithms

$$\ln p(Z) = \ln C + N\ln(\delta\omega) - m\ln(2\pi) + (N+\tfrac{1}{2})\ln N - \sum_\nu (f_\nu+\tfrac{1}{2})\ln f_\nu \quad . \tag{4.305}$$

As we have done before in Chapter III we express the logarithms of the $f_\nu$ as series expansions in powers of $(f_\nu - f_\nu^0)/f_\nu^0$, which quantities are assumed to be small as compared to unity since the $f_\nu$ and $f_\nu^0$ are both large and of the same order of magnitude, while we are still interested in situations reasonably close to the

equilibrium one. Neglecting higher powers than the second in this expansion, we obtain upon rearrangement;

$$p(Z)=C(\delta\omega)^N(2\pi)^{-m_N N+\frac{1}{2}}e^{-\sum_\nu[(f_\nu-f_\nu^e)^2/2f_\nu^e+f_\nu \ln f_\nu^e+\frac{1}{2}\ln f_\nu^e]}. \tag{4.306}$$

This expression is constant apart from the first two terms in the exponent. As we have already mentioned the system is an isolated one, and will have a constant total energy, E, which we express as the sum

$$E = \sum_\nu \epsilon_\nu f_\nu \quad , \tag{4.307}$$

where $\epsilon_\nu$ is assumed to be the energy associated with a particle in the vth cell. It is well known (e.g. compare ter Haar 1954, chap. II) that the equilibrium distribution of such a system is given by the Maxwell-Boltzmann distribution

$$f_\nu^e = N\delta\omega e^{\nu-\mu\epsilon_\nu} \quad , \tag{4.308}$$

where $\nu$ and $\mu$ are constants of the system. Substituting for $\epsilon_\nu$ in equation (4.307) and recollecting that $\sum_\nu f_\nu^e = N$, we have the equation

$$(\nu+\ln N+\ln\delta\omega)N-\mu E = \sum_\nu f_\nu \ln f_\nu^e \quad . \tag{4.309}$$

The left hand side of this equation is composed of constant terms so that the sum on the right is constant also. Hence the only variable left in the expression for p(Z) is that sum which we now denote by $\Delta$ ;

$$\Delta = \sum_\nu (f_\nu-f_\nu^e)^2/2f_\nu^e \quad . \tag{4.310}$$

For $p\{f_v\}$ to be normalized the constant C must have the value given by

$$C = (N\delta\omega)^{-N_e} \, e^{-\sum_v f_v \ln f_v^e} \quad . \tag{4.311}$$

Substituting from equations (4.310) and (4.311) into equation (4.306) we have

$$p(Z) = N^{\frac{1}{2}} (2\pi)^{-m} \left\{\prod_v f_v^e\right\}^{-\frac{1}{2}} e^{-\Delta} \quad . \tag{4.312}$$

Now $\Delta$ is zero if and only if the set $\{f_v\}$ is the equilibrium one, so that from equation (4.304) it is seen that $\Delta$ satisfies equation (4.301). However this is only an approximation due to the assumptions which we have made concerning the magnitudes of the $f_v$ and $f_v^e$.

The conditional probability $p\{f_v\}$ is identical with $p(Z)$ and is also given by equation (4.312). To complete the information needed in order to perform our calculations we require only the probabilities of the stochastic variables $x_{vv'}$, introduced by equation (4.110). We may again plausibly assume that the distribution of these random variables is bernoullian (compare Chap.V, §3). Remembering that their averages are given by $a_{vv'}, f_v$, and that from the last section we may take

$$N \gg a_{vv'}, N \gg 1 \quad , \tag{4.313}$$

then as in the case of the wind-wood model we can approximate to the bernoullian distribution by the gaussian one $p(x_{vv'})$, so that

$$p(x_{vv'}) = (2\pi a_{vv'} f_v)^{-\frac{1}{2}} e^{-(x_{vv'}-a_{vv'}f_v)^2/2f_v a_{vv'}} \quad . \quad (4.314)$$

We should again remark that the assumption of the bernoullian distribution is an important one, and is connected with the manner in which the time scale is chosen. This point will be discussed later.

§4. Evaluation of the Formulae.

Once more we have obtained the expressions necessary for us to be able to make use of the Markoff-Chandrasekhar method of evaluating the probabilities $w(\Delta)$ and $w(\Delta,\Delta')$.

For the calculation of $w(\Delta)$ we have $\Delta$ defined by equation (4.310) and so the transform $A(\rho)$ is defined by

$$A(\rho) = \int\cdots\int p\{f_v\}\, e^{\sum_v i\rho(f_v-f_v^e)^2/2f_v^e} df_{-m}\ldots df_{+m} \quad . \quad (4.401)$$

Since the $f_v$ are connected by relation (4.105) the integration is to be performed over $2m$ variables, where we have chosen to express $f_0$ in terms of the rest of the set $\{f_v\}$. Substituting for $f_0$, and for $p\{f_v\}$ from equation (4.312) we have

$$A(\rho) = N^{\frac{1}{2}}(2\pi)^{-m}\left\{\prod_v f_v^e\right\}^{-\frac{1}{2}} \qquad (4.402)$$

$$\int\cdots\int \exp -\tfrac{1}{2}(1-i\rho)\left[\sum_{v\neq 0}\left(\frac{1}{f_{10}^e}+\frac{1}{f_{1v}^e}\right)(f_v-f_v^e)^2+\frac{2}{f_{10}^e}\sum_{\substack{v<v'\\ \neq 0}}(f_v-f_v^e)(f_{v'}-f_{v'}^e)\right] df_{-m}\ldots df_{+m}.$$

The symbols $\sum_{v\neq 0}$ and $\sum_{\substack{v<v'\\ \neq 0}}$ denote summations over all values of v except $v=0$, and in the second case a double summation where $|v|<|v'|$. The integrals are taken from

$-\infty$ to $+\infty$ for the reasons stated in Chapter III. Performing these integrations, we obtain

$$A(\rho) = (1-i\rho)^{-m} \quad . \tag{4.403}$$

Then from equation (3.211) the probability $w(\Delta)$ will be given by

$$w(\Delta) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} (1-i\rho)^{-m} e^{-i\rho\Delta} d\rho \quad , \tag{4.404}$$

and after evaluation of the simple contour integral involved we have the result

$$w(\Delta) = \frac{\Delta^{m-1}}{(m-1)!} e^{-\Delta} \quad . \tag{4.405}$$

This probability is normalized with respect to $\Delta$, and the average value of $\Delta$ is

$$\Delta_{av} = \int \Delta\, w(\Delta) d\Delta = m \quad . \tag{4.406}$$

If $m = 3/2$, equation (4.405) goes over into the expression for $w(\Delta)$ found for the wind-wood model.

The change in $\Delta$ during $\tau$ due to collisions, $\delta\Delta = \Delta - \Delta'$, is related to the variations in the $f_v$ by the following equation derived from the definition of :

$$\delta\Delta = \sum_v (f_v - f_v^e)\, \delta f_v / f_v^e = \sum_v \delta f_v . f_v / f_v^e \quad . \tag{4.407}$$

The last expression holds because $\sum_v \delta f_v = 0$. The differential equations (4.111) give the variations in $f_v$ as

$$\delta f_v = \sum_{v'} (x_{v'v} - x_{vv'}) \quad . \tag{4.408}$$

Following the same procedure as in Chapter III, §3, we set up the bivariate transform $A(\xi,\sigma)$ where

$$A(\xi,\sigma) = \int\cdots\int p\{f_v\} \prod_{v,v'} p(x_{vv'}) \qquad (4.409)$$

$$\exp\left[i\xi\sum_v f_v \delta f_v/f_v^e + i\sigma\sum_v (f_v - f_v^e)^2/2f_v^e\right] df_{-m}\ldots dx_{mm}.$$

We substitute the expressions for $p\{f_v\}$ and $p(x_{vv'})$ from equations (4.312) and (4.314) and perform the simple integrations over the $(2m+1)^2$ variables $x_{vv'}$ with limits $-\infty$ to $+\infty$. The result is of the form

$$A(\xi,\sigma) = N^{\frac{1}{2}}(2\pi)^{-m}\left\{\prod_v f_v^e\right\}^{-\frac{1}{2}}\int\cdots\int e^{E}\, df_{-m}\ldots df_{+m}\,, \qquad (4.410)$$

where

$$E = \sum_v\sum_{v'} \tfrac{1}{4}a_{vv'}f_v\left[\left\{1+i\xi\left(\frac{f_v}{f_v^e}-\frac{f_{v'}}{f_{v'}^e}\right)\right\}^2-1\right] \qquad (4.411)$$

$$+\tfrac{1}{2}(1-i\sigma)\left[\sum_{v\neq 0}\alpha_v^2\left(\frac{1}{f_0^e}+\frac{1}{f_v^e}\right)+\frac{2}{f_0^e}\sum_{\substack{v<v'\\ \neq 0}}\alpha_v\alpha_{v'}\right]\,,$$

where we have introduced the variables $\alpha_v$ by $\alpha_v = f_v - f_v^e$. The fact that the $f_v^e$ are no longer constant complicates the calculations, but by using the detailed balance relation which ensures that $a_{v'v}f_{v'}^e = a_{vv'}f_v^e$ we can reduce this expression to

$$E = \sum_{v<v'} a_{vv'}f_v^e\left(\frac{\alpha_v}{f_v^e}-\frac{\alpha_{v'}}{f_{v'}^e}\right)^2\left[1\xi-\tfrac{1}{2}\xi^2\left(\frac{\alpha_v}{f_v^e}+\frac{\alpha_{v'}}{f_{v'}^e}+2\right)\right] \qquad (4.412)$$

$$-\tfrac{1}{2}(1-i\sigma)\left[\sum_{v\neq 0}\alpha_v^2\left(\frac{1}{f_0^e}+\frac{1}{f_v^e}\right)+\frac{2}{f_0^e}\sum_{\substack{v<v'\\ \neq 0}}\alpha_v\alpha_{v'}\right]\,,$$

and then using the fact that the $\alpha_v$ are dependent, and that

$$\alpha_0 = -\sum_{v\neq 0}\alpha_v\,,$$

we obtain

$$E = -\sum_{v\neq 0}\alpha_v^2\left[\rho(\rho+i)\left(\frac{\sum_{r\neq 0,v} a_{vr}}{f_0^e}+\frac{\sum_{s\neq v} a_{vs}}{f_v^e}+\frac{2a_{ov}}{f_0^e}\right)+\frac{1}{2}(1-i\sigma)\left(\frac{1}{f_0^e}+\frac{1}{f_v^e}\right)\right]$$

$$-2\sum_{\substack{v<v'\\ \neq 0}}\alpha_v\alpha_{v'}\left[\rho(\rho+i)\left(\frac{\sum_{v\neq 0} a_{ov}}{f_0^e}-\frac{a_{vv'}}{f_v^e}+\frac{a_{ov}}{f_v^e}+\frac{a_{ov'}}{f_{v'}^e}\right)+\frac{1}{2}(1-i\sigma)\frac{1}{f_0^e}\right]. \tag{4.413}$$

At this point in order to proceed further we must consider the particular forms of $a_{vv'}$, proper to the various models with which we are concerned. If $a_{vv'}$, depends only upon v' or is a constant, then equation (4.413) reduces again to

$$E = -\left[A\rho(\rho+i)+\frac{1}{2}(1-i\sigma)\right]\left[\sum_{v\neq 0}\alpha_v^2\left(\frac{1}{f_0^e}+\frac{1}{f_v^e}\right)+\sum_{\substack{v<v'\\ \neq 0}}\alpha_v\alpha_{v'}\cdot\frac{2}{f_0^e}\right] \tag{4.414}$$

where

$$A = \sum_v a_{0v} \quad . \tag{4.415}$$

If $g_v$ is constant and $p(v,v')$ is a symmetric function, we see from the examples in section 3 that $a_{vv'}$ will be small and will alter little so that to a fair degree of approximation we may take $\sum_{v'} a_{vv'}$, to be equal to $g/(2m+1)$ where $g$ is the constant value of $g_v$. Thus, since $f_v^e$ is constant in this case we can write E as

$$E = -\left[\frac{2A}{f_v^e}\rho(\rho+i)+(1-i\sigma)\frac{1}{f_v^e}\right]\left[\sum_{v\neq 0}\alpha_v^2+\sum_{\substack{v<v'\\ \neq 0}}\alpha_v\alpha_{v'}\right] \quad , \tag{4.416}$$

where now

$$A = 2g/(2m+1) \quad . \tag{4.417}$$

Substituting either of the expressions (4.414) or (4.416) for E in equation (4.410), replacing the 2m variables $f_\nu$ by the $a_\nu$ and integrating over these variables from $-\infty$ to $+\infty$ gives the result

$$A(\varsigma,\sigma) = [2A\varsigma(\varsigma+i)-i\sigma+1]^{-m} \quad . \tag{4.418}$$

The equivalent of equation (3.218) is now

$$w(\Delta)w(\Delta,\Delta') = \frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\int [2A\varsigma(\varsigma+i)-i\sigma+1]^{-m} e^{-i\varsigma\Delta - i\sigma\Delta} \, d\varsigma \, d\sigma \quad . \tag{4.419}$$

Since m is now an integer two simple contour integrations suffice to give the result, after dividing by $w(\Delta)$, that

$$w(\Delta,\Delta') = (8\pi A\Delta)^{-\frac{1}{2}} e^{-(\Delta'-\Delta+2A\Delta)^2/8A\Delta} \quad . \tag{4.420}$$

This is normalized with respect to $\Delta'$, and from it we obtain the average value of $\Delta'$:

$$\Delta'_{av} = \int \Delta' w(\Delta,\Delta') d\Delta' = (1-2A)\Delta \quad . \tag{4.421}$$

Hence the average rate of change of $\Delta$ with time is

$$(d\Delta/dt)_{av} = (\Delta'_{av}-\Delta)/\tau = -2A\Delta/\tau \quad . \tag{4.422}$$

The recurrence probability is got from $w(\Delta,\Delta')$ by putting $\Delta' = \Delta$. So

$$w(\Delta,\Delta) = (8\pi A\Delta)^{-\frac{1}{2}} e^{-\frac{1}{2}A\Delta} \quad . \tag{4.423}$$

The mean life and the average time of recurrence appear directly from the formulae derived in Chapter II following the substitution in them of the above

expressions for $w(\Delta)$ and $w(\Delta,\Delta)$. Hence

$$T(\Delta) = \tau[1-(8\pi A\Delta)^{-\frac{1}{2}}e^{-\frac{1}{2}A\Delta}]^{-1}$$

$$\simeq \tau \quad ; \qquad (4.424)$$

and

$$\Theta(\Delta) \simeq \tau/w(\Delta)$$

$$= \tau\, e^{\Delta}\Delta^{-m+1}(m-1)! \quad . \qquad (4.425)$$

The remarks on the similar expressions quoted at the end of Chapter III are true for these also. It should be noted that the two sets of expressions are not exactly equivalent, for in the case of the wind-wood model m would have the value 3/2, so that m would be too small to make the approximation used in deriving equation (4.416) at all reliable. Otherwise the results are general, certainly as far as the form of the expressions is concerned, while it will be seen that both the quantities $T(\Delta)$ and $\Theta(\Delta)$ are approximately independent of A.

## Chapter V

### §1. The H-theorem Curve.

In this chapter we will discuss the behaviour of the curves describing the variation of H with time. Firstly we consider the models in the light of the Stosszahlansatz, so that H will be governed by the unrestricted H-theorem, and thus $dH/dt \leq 0$. The differential equations for $df_v/dt$ given by equations (3.105) and (4.106) show that the $f_v$ tend exponentially to the equilibrium values $f_v^e$. As we have mentioned before however, the quantity $\Delta$ (and hence also H) is not determined uniquely by a set $\{f_v\}$, except in the case of the Wind-Wood model in one dimension. Due to the fact that we have in general 2m+1 variables $f_v$ and only the one restriction that the sum of these should be N, it is evident that a particular value of $\Delta$, which is defined essentially as the sum of the squares of the $f_v$;

$$\Delta = \sum_v f_v^2/2f_v^e - \tfrac{1}{2}N \quad , \qquad (5.101)$$

should be attainable from different sets $\{f_v\}$. We therefore must take an average over all such sets equivalent to one value of $\Delta$ in order to describe the variation $d\Delta$ uniquely in terms of the $f_v$. Denoting this

average by square brackets we have

$$[\Delta]_{av} = \Delta = [\sum_{v} f_v^2/2f_v^e]_{av} - \tfrac{1}{2}N \quad . \qquad (5.102)$$

From this we have the useful identity

$$[\sum_{v} f_v^2/2f_v^e]_{av} = \sum_{v} f_v^2/2f_v^e \quad . \qquad (5.103)$$

The rate of change of $\Delta$ is given by

$$d\Delta/dt = \sum_{v} \frac{df}{dt} v . f_v/f_v^e \qquad (5.104)$$

where the expressions for the $df_v/dt$ are those of equation (4.106). Thus

$$d\Delta/dt = (1/\tau)\sum_{v}\sum_{v'} f_v(a_{v'v}f_{v'} - a_{vv'}f_v)/f_v^e \quad . \qquad (5.105)$$

The detailed balancing condition (4.109) allows us to express $a_{v'v}$ in terms of $a_{vv'}$, with the result that

$$d\Delta/dt = -(1/\tau)\sum_{v}\sum_{v'} (a_{vv'}f_v^2/f_v^e - a_{vv'}f_v f_{v'}/f_{v'}^e) \quad . \qquad (5.106)$$

We now take the two terms on the right hand side of this equation separately. For the first, after summing over v' and recollecting that $\sum_{v'} a_{ov'} = A$ according to equation (4.415), we have

$$-(A/\tau)\sum_{v} f_v^2/f_v^e = [-(A/\tau)\sum_{v} f_v^2/f_v^e]_{av} \quad , \qquad (5.107)$$

by virtue of equation (5.103).

The second term may be divided into two parts by introducing once more the variables $a_v$ in place of the $f_v$. First of all however, assuming that $a_{vv'}$ is either constant or depends upon v' only, we may sum over v,

obtaining

$$\sum_{v}\sum_{v'} a_{vv'}f_v f_{v'}/f^e_{v'} = N\sum_{v'} a_{vv'}f_{v'}/f^e_{v'}$$

$$= N\sum_{v'} a_{vv'}(1+[a_{v'}/f^e_{v'}])$$

$$= N\Delta + N\sum_{v'} a_{vv'}a_{v'}/f^e_{v'} \quad . \qquad (5.108)$$

But $a_{vv'}/f^e_{v'}$ is constant, and since $\sum_v a_v = 0$ the last term disappears. Thus if we take the average over the equivalent sets the result is simply

$$[(1/\tau)\sum_{v}\sum_{v'} a_{vv'}f_v f_{v'}/f^e_{v'}]_{av} = N\Delta/\tau \quad . \qquad (5.109)$$

The average rate of change of $\Delta$ is then given by equations (5.106),(5.107) and (5.109) as

$$[d\Delta/dt]_{av} = -(\Delta/\tau)\sum_{v}(f_v^2/f^e_v - N)$$

$$= -2\Lambda\Delta/\tau \quad . \qquad (5.110)$$

We have so far ignored the cases where $a_{vv'}$ is symmetric but not constant. Once again in such cases we take as an approximation the value of $\Lambda$ to be constant and equal to $2g/(2m+1)$. The irregularity of the function $a_{vv'}$ for the wind-wood model spoils the generality, but by direct calculation along the above lines we can derive the result already quoted in equation (3.116), i.e.

$$[d\Delta/dt]_{av} = -4g\Delta/\tau \quad .$$

The H-theorem curve is thus defined by the initial

value of H at time $t = 0$, say $H_A = H_{min} + \Delta_A$, and by the rate of change

$$dH/dt = -2A(H - H_{min})/\tau \quad . \qquad (5.111)$$

The curve thus described declines steadily from the value $H_A$ and tends exponentially to the minimum value $H_{min}$. We call this the H-theorem curve, and in the next section it will be shown how the same curve may be obtained even after the Stosszahlansatz has been abandoned, by taking averages in accordance with the conditions of the restricted H-theorem.

## §2. The $\eta$-curve.

In order to determine the average behaviour of the function H we must distinguish carefully between two possible procedures. In the first place we could take the value of $(d\Delta/dt)_{av}$ as given by equation (4.422) and observe that it has the same value as that obtained for $[d\Delta/dt]_{av}$ in the last section. One might then deduce from this that since the average value of dH/dt is negative or zero, and has the same magnitude as that obtained for the unrestricted case with the Stosszahlansatz in force, that therefore the result of abandoning the Stosszahlansatz is that the variation of H given by the original theorem appears as the average of the true variation. This would follow of course from the

idea of the Stosszahlansatz values of the collisions as being averages of the true values. This approach must be regarded with some suspicion especially since the average of $d\Delta/dt$ in question is obtained by averaging over all values of $\Delta'$, the final value at the end of the interval $\tau$. Since this value is also the initial one for the next time interval we might expect difficulties to occur because we have taken no account of this, and have regarded each step as being independent.

It would appear then to be more correct to consider the system in a strictly statistical mechanical way as a member of an ensemble, and to deal with the averages as averages taken over this ensemble. The ensemble is formed by considering the situation characterized by the quantity $H_A$ at a time $t_A$. As explained in the first chapter there will be many states which give rise to the same value $H_A$ thus defining an 'H-star' of volume $W(H_A)$ analogous to the Z-star which we had previously. H has now replaced Z as the variable describing the state of the system. The collective of similar systems with the same total energies and numbers of particles which have states lying in the $H_A$-star form an ensemble. From what has gone before it is possible to calculate the distribution of their subsequent H values at later times, and thus to obtain the averages taken over the ensemble.

Before doing this it is convenient to derive some necessary expressions. The probabilities $w(H)$ and $w(H,H')$ follow from equations (4.405) and (4.420) for $w(\Delta)$ and $w(\Delta,\Delta')$ since we have that $H = H_{min} + \Delta$. Thus

$$w(H) = (H-H_{min})^{m-1} e^{-H+H_{min}}/(m-1)! \quad \text{if } H \geqslant H_{min},$$
$$= 0 \quad \text{otherwise,} \tag{5.201}$$

and

$$w(H,H') = [8\pi A(H-H_{min})]^{-\frac{1}{2}} e^{-[H+2A(H-H_{min})]^2/8A(H-H_{min})}$$
$$\text{if both } H \text{ and } H' \geqslant H_{min},$$
$$= 0 \quad \text{otherwise,} \tag{5.202}$$

where A is positive and much less than unity. It should be remembered that $W(H)$ is the volume of the H-star, and is not a probability as is $w(H)$. From the latter of these two equations it follows that

$$\int w(H,H')dH' = 1 \quad . \tag{5.203}$$

In addition we have the useful results that

$$\int H' w(H,H')dH' = (1-2A)(H-H_{min}) + H_{min} \quad , \tag{5.204}$$

and

$$\int H'^2 w(H,H')dH' = [(1-2A)(H-H_{min}) + H_{min}]^2 \quad . \tag{5.205}$$

These are true to the first order of magnitude in A, the integrations having been performed by the method of steepest descents (Appendix, §1).

Denoting the value of H at a time $t_\Lambda + n\tau$ by $H_n$,

the probability distribution of $H_n$ is

$$w(H_n) = w(H_A)w(H_A,H_1)w(H_1,H_2)\ldots w(H_{n-1},H_n) \quad . \qquad (5.206)$$

We define the average $\eta_n$, taken over the ensemble, of all the H values at time $t_A + n\tau$ as

$$\eta_n = \frac{1}{w(H_A)} \int\ldots\int w(H_n)H_n dH_1 dH_2 \ldots dH_n \qquad (5.207)$$

following the definition given by the Ehrenfests (1911, 14). From equations (5.204) and (5.206) we obtain that

$$\eta_n = (1-2A)H_A + 2AH_{min} \sum_{r=0}^{n-1} (1-2A)^r$$

$$= (1-2A)^n(H_A - H_{min}) + H_{min} \quad . \qquad (5.208)$$

Since the time scale is given by $t = n\tau$ we then have the $\eta$-curve;

$$\eta(t/\tau) = H_{min} + (1-2A)^{t/\tau}(H - H_{min}) \quad . \qquad (5.209)$$

This is an exponential curve which, starting with the value $H_A$, then decreases steadily to the value $H_{min}$. The rate of change is given by

$$d\eta/dt = -2A(\eta_n - H_{min})/\tau \quad , \qquad (5.210)$$

again to the first power in A. Comparing this result with the expression (5.111) for the H-theorem curve we see that these two curves are identical in all respects. Thus we may say that the quantity $\eta_n$ defined as an average over the ensemble obeys the unrestricted

H-theorem even though we have abandoned the Stosszahlansatz in order to obtain it.

Finally it may be noted that the dispersion of H values about the mean value $\eta_n$ is very small. For if we define the dispersion $\mathcal{D}_n$ by

$$\mathcal{D}_n = \frac{1}{w(H_A)} \int\cdots\int w(H_n)(\eta_n - H_n)^2 dH_1 \ldots dH_n \quad , \quad (5.211)$$

then using equation (5.205) we obtain the result that

$$\mathcal{D}_n = 0 \quad , \quad (5.212)$$

at least to the first power in $\Lambda$.

## §3. The Nature of the Process.

We have not so far identified the process which is described by the variation of H with respect to time with any particular recognised type. It is important however, to go more deeply into this question since it affects the validity of some of our formulae.

To start with we will use the ideas of the previous section to recapitulate our knowledge of this process in terms of ensembles. To do this we must consider the question of the actual observations which would give us our information relating to the system. Suppose that we have an isolated system about which we have no previous knowledge as to its history, and that we observe it at a time $t_A$, thus obtaining a value $H_A$. We further assume

that $H_A$ is much larger than $H_{min}$. We must now set up an ensemble of systems each of which satisfy the conditions leading to $H_A$ at $t_A$, and each of which has the same a priori probability. This has to be done because we must use statistical mechanical methods since due to our division of phase space we do not have exact information about the system. We then obtain a negative average value of $dH/dt$ for the members of the ensemble. The value of H at some subsequent time $t_B$ then follows from

$$H_B = H_A + (dH/dt)_{av}(t_B - t_A) \qquad (5.301)$$

as long as $t_B - t_A$ is so short that higher order terms may be neglected. Thus we may predict that for such short times $H_B$ will be less than $H_A$.

Now suppose that we actually make the observation at $t_B$ and thus obtain $H_B$. This value will presumably differ from the estimated value given by equation (5.301) but at any rate it is still very likely to be less than $H_A$. We now set up a new representative ensemble such that all its members are in states which conform to the conditions observed at time $t_B$, although each member has once again the same a priori probability. Starting with this ensemble at time $t_B$ we may again predict a negative value for $dH/dt$ so that $H_C$ at a slightly later time $t_C$ should be less than $H_B$. Continuing in this way

we can argue that it is highly probable that the values of H corresponding to successive observations on the system become smaller and smaller.

This method of approach is open to criticism on the grounds that although it is correct to construct the ensemble corresponding to the value $H_A$, it is not legitimate to do the same for the later time $t_B$ because we now have knowledge of the previous history of the system. The ensemble at $t_B$ could in principle be built up in such a way as to include the information that we have of the situation at $t_A$. It would be necessary to exclude from this ensemble the representative points of all systems which could not have come from the known situation at $t_A$ to that at $t_B$ in the time $t_B - t_A$. One can easily imagine the complications involved in such a correction, and the amount of exact specification of the orbits of the representative points necessary would seem to put it outside the field of the statistical mechanical method. We may conclude with Tolman (1938, §49) that it is reasonable to suppose that the representative points of such systems as must be excluded from the second ensemble can be regarded as scattered amongst the members of the $H_B$-star in such a random manner that they do not affect our prediction of a negative value of $d\bar{H}/dt$ on average over the members of the ensemble.

The above conclusions have particular relevance in connection with the question of whether or not the process is a markovian one. We may find the probability of a state $H_r$, as in section 2, as the product of the initial probability and of the transition probabilities. The transition probabilities $w(H_{r-1},H_r)$ appear to satisfy the requirements for the elements of a Markoff chain matrix in as much as they depend only upon $H_r$ and the preceding state $H_{r-1}$. Going into more detail it will be recollected that in order to introduce the fluctuations about the Stosszahlansatz values we assumed that the stochastic variables $x_{vv'}$ were randomly distributed about the Stosszahlansatz value as a mean. However the mean value $a_{vv'}f_v(t)$ (see equation 4.110) will in general change after the expiry of each element of time $\tau$. We have therefore assumed that it is possible to neglect any influence that the distribution of the previous time element might have on its successor, apart from the change in the mean which gives the new value $a_{vv'}f_v(t+\tau)$. The procedure is a reflexion in miniature of that one we have just discussed concerning H. For here we could take the fluctuation variables $x_{vv'}$ as forming a kind of ensemble, with average $a_{vv'}f_v(t)$, and just as above we could set up a new ensemble at the start of each interval $\tau$. The assumption that no

allowance need be made for the previous history of the process is equivalent to the action of randomizing the $x_{vv}$, afresh for each $\tau$. Further, the assumption of equal a priori probabilities for the members of the ensemble justifies the use of the Bernoulli distribution for $x_{vv}$, (equation 4.314).

It has thus been shown that although the process is not actually markovian to the extent that each link in the chain is dependent only upon its predecessor, yet it may plausibly be assumed to behave like one, to a fair degree of approximation. This leads us to a criticism made by Bartlett (1950,1953) of the formulae given by Chandrasekhar (1943), and derived in Chapter II, § 2 of this thesis. In obtaining equation (2.210) for the average time of recurrence Chandrasekhar had used arguments involving the behaviour of the states not n, or $\underline{n}$. But even although n is a state in a markovian chain, $\underline{n}$ is not, for the system can be shown to have a memory of earlier $\underline{n}$ states. This corresponds exactly to the question of taking account of those states in the ensemble which do not belong to the $H_A$-star but which do belong to the $H_B$-star. Bartlett shows that values obtained for the recurrence times in this way will be incorrect unless the previous history of such states is included in the probability matrix. However he also shows that if the average values are taken results are

obtained which are to all intents and purposes the same as the formulae (2.203) and (2.210) for $\Gamma(n)$ and $\Theta(n)$. This fact might also be adduced to confirm to some extent the validity of neglecting what we might call the non-markovian states in the ensembles, since it shows that in one case at any rate that these non-markovian terms have little effect upon the average values.

In the discussion of the urn model in Chapter II it was mentioned that in order to be able to neglect the initial distribution of the balls over the two urns it was necessary to assume that the equilibrium state $\Delta=0$ had occurred at least once before the time at which the first observation was made. The difficulty arises again in the general case when we come to define the probability of the state Z. We obtained an expression for p(Z) in equation (4.303) which depended only upon the values of the occupation numbers of the state Z and had no reference to the intial state of the system at time t=0. It would appear from the work of Siegert (1949) that this procedure requires justification. Siegert has considered the same class of models but adheres throughout to a Stosszahlansatz which is a more general one than that which we have used. In Siegert's usage the word Stosszahlansatz denotes any assumption which gives the probability of a change in Z in the small time $\tau$ in

terms of the sets or matrices $\{f_v\}$ and $\{a_{vv'}\}$. Having set up by these means the matrix of the Markoff process with states Z, he calculates the probability $p(Z_o, Z_t)$ that the state Z which had at the time t=0 the value $Z_o$ should have the value $Z_t$ at time t. He then shows for several models in this class that as $t \to \infty$ then $p(Z_o, Z_t)$, becomes independent of $Z_o$ the initial configuration, and depends only upon $Z_t$. What is more, the value of $p(Z_t)$ thus found is just that one which we have denoted by p(Z). It would thus appear that once the equilibrium situation corresponding to $\Delta = 0$ has occurred, that we can then use expression (4.303) for p(Z) with justification. In other words, as we have indicated already, we are actually investigating what are primarily fluctuations about the equilibrium situation.

# Chapter VI

## §1. The Poincaré Cycle.

The principal value of the detailed investigation which we have carried out in the preceding chapters must lie in the fact that the results obtained admit of quantitative interpretation. The general theory of the approach of a system to equilibrium is of such generality that it is difficult to obtain from it an idea of the magnitude of the effects that it predicts. Without knowledge of such magnitudes it is impossible to tell whether or not these effects will be observable in nature. For example the information that $dH/dt$ is less than or equal to zero is given by the theory, yet in general it is not possible to obtain an idea of the time required to reach equilibrium without reference to the specific mechanism of the system. It is for this reason that it should be of interest to consider even such simplified models as those we have treated.

There are certain quantities whose magnitudes are especially important to the study of the time dependence of isolated systems. One of these is the period of the Poincaré cycle. In Chapter I we introduced Poincaré's Theorem as stating that an isolated mechanical system

performs some sort of periodic motion as its representative point in $\Gamma$-space describes orbits over its energy surface. We define the period of such motion as the average time required for the representative point to return to the neighbourhood of its initial position after having in the meantime passed through all points on the energy surface. It must be emphasized that this period is not the same as the average time of recurrence of the initial state, for in the second case there is no necessity for the orbit to pass through all the other possible states. The Poincaré period is obviously enormously long. Its exact determination for our models is not easy, involving as it does the treatment of a random walk process with variable $\Delta$, and with two reflecting barriers at $\Delta = 0$ and at $\Delta = \Delta_{max}$. However we may obtain an estimate of its value by comparing the definitions of the period and of the mean recurrence time. We do this by finding the time necessary for the system to pass through all possible values of and then to recur to the initial value. Considering the form of the $\Delta$-curve which describes the variation of the system we see that during this time it must have reached the extreme values $\Delta = 0$ and $\Delta = \Delta_{max}$. Having done so, it has then of necessity passed through all the intermediate values, since $\Delta$ may only alter by one step

during each element $\tau$. Thus the Poincaré period must be of the same order of magnitude as that of the average time of recurrence of the maximum value of $\Delta$, that is $\Theta(\Delta_{max})$. From the form of $\Theta(\Delta)$ [equation (4.425)] it can be seen that for moderate values of $\Delta$ the Poincaré period $\Theta_p$ will be vastly longer than the average time of recurrence.

It would be instructive to compare the magnitude of this period with that of the relaxation time required for a system to reach equilibrium. The definition of this latter quantity must be somewhat arbitrary because $\Delta$ approaches $\Delta = 0$ asymptotically. We will however take the relaxation time $R(\Delta)$ as being the average time required for the system to decline from $\Delta$ to a value $\Delta_0$, where $\Delta_0$ differs from zero only by the small amount obtained by putting $f_v = f_v^0 + 1$ in the definition of $\Delta$. This should be sufficiently small, for the $f_v$ are certainly large. The average rate of change of is given by equation (4.422) as

$$d\Delta/dt = -2A\Delta/\tau \ ,$$

so that the relaxation time is

$$R(\Delta) = \frac{\tau}{2A} \ln (\Delta/\Delta_0) \ . \qquad (6.101)$$

This will undoubtedly be very large as compared to $\tau$.

Tolman (1938, § 51) and the Ehrenfests (1911, § 23)

express completely opposite opinions concerning the magnitude of the relaxation time. The latter expected that the relaxation time would be of the order of magnitude of the Poincaré period, and thus, presumably, exceedingly large as compared to the time of observation. Tolman takes the view that the relaxation time will be shorter than this, and that if the phase cells are enlarged so as to approach the limit of experimental measurements then the relaxation time should become very small.

In order to throw some light on this problem we will consider a particular model. For the sake of simplicity we take the Lorentz model of Chapter IV, and give the various constants the following values:

$$\begin{aligned} N &= 10^{24} \quad ; \quad n = 10^{20} \\ m &= 10^{4} \quad ; \quad \sigma = 10^{-12}\ \text{cm}^{-1} \\ c &= 10^{6}\ \text{cm sec}^{-1} \quad ; \quad \tau = 10^{-17}\ \text{sec} \ . \end{aligned} \tag{6.102}$$

As a result we have for g the value

$$g = nc\sigma\tau = 10^{-2} \ , \tag{6.103}$$

and thus for A,

$$A = g/(2m+1) = \tfrac{1}{2}.10^{-6} \ . \tag{6.104}$$

The value of $\tau$ has been of course chosen so that $g \ll 1$.

The maximum value of $\Delta$ occurs when all the particles are moving in the one direction (perfect order) and is

given by the definition of $\Delta$ of equation (5.101) as

$$\Delta_{max} = mN \quad . \tag{6.105}$$

We obtain the value of $\Delta_o$ by supposing that each occupation number $f_v$ differs from its equilibrium value by unity, so that

$$\Delta_o = \sum_v 1/2 f_v^e = 2m^2/N \tag{6.106}$$

since $f_v^e = N/(2m+1)$ for this model. Substituting this value into equation (6.101) we obtain for the relaxation time the expression

$$R(\Delta) = \frac{\tau}{2A} \ln (N\Delta/2m^2) \quad . \tag{6.107}$$

Comparing this with the expression for the Poincaré period as $\textcircled{H}(\Delta_{max})$, or

$$\textcircled{H}_p = \textcircled{H}(mN) \simeq e^{mN} m!(mN)^{-m} \quad , \tag{6.108}$$

where we have used equation (4.425), we observe that except possibly for very large $\Delta$ the period will be very much longer than the relaxation time. For example if we compare the period with the relaxation time of the state with $\Delta = \Delta_{av} = m$, we have

$$R(\Delta_{av}) \sim 2.10^{-10} \text{ sec} \quad ,$$

$$\textcircled{H}_p \sim 10^{10^{10}} \text{ sec} \quad .$$

It might be argued that the definition of the relaxation time is artificial, and that $\Delta_o$ should be smaller, thus increasing $R(\Delta)$, but from our definition of the size of

the phase cells it is evident that $\Delta_o$ could be taken to be much larger and it would still be indistinguishable from the equilibrium value for all practical purposes. If the phase cells were to be increased in size this would be even more plausible, while the decrease in m would contribute to a reduction in the relaxation time, in accordance with the views of Tolman.

As far as the apparent reversibility of the system is concerned the times of recurrence are so large that there is little likelihood of detecting the reversible nature of the process. The value of $\tau$ quoted for the Lorentz model is of course far smaller than the times dealt with experimentally, but there is no reason why one should not consider the observations as being made after the expiry of periods of time consisting of many elements $\tau$. This would correspond to the state of affairs in the H-curve shown in figure 2 where $\Delta t$ could be many times larger than $\tau$. Previously we have taken $\Delta t$ to be equal to $\tau$.

It may be shown that the process is in fact reversible with respect to the direction of the time scale. Suppose we consider a peak of height $\Delta$ in the $\Delta$-curve, and that the values of $\Delta$ which occur at intervals $\tau$ before and after this are $\Delta''$ and $\Delta'$ respectively. Then by summing over all possible values of $\Delta''$ and $\Delta'$ we can obtain the average values of these quantities. Thus

$$\Delta'_{av} = \int w(\Delta,\Delta')\Delta' \, d\Delta' \quad , \tag{6.109}$$

and

$$\Delta''_{av} = \frac{\int w(\Delta'')w(\Delta'',\Delta)\Delta'' \, d\Delta''}{\int w(\Delta'')w(\Delta'',\Delta)d\Delta''} \quad . \tag{6.110}$$

Using the expressions for $w(\Delta)$ and $w(\Delta,\Delta')$ already derived in Chapter IV and integrating approximately by the method of steepest descents, we obtain the result that to the first power in $\Lambda$;

$$\Delta'_{av} = \Delta''_{av} = (1-2\Lambda)\Delta \quad . \tag{6.111}$$

It follows from this that $\Delta$ will decrease at the average rate of $-2\Lambda\Delta/\tau$ whether we take the time scale as increasing to the right or to the left, and that therefore the process is reversible. It may be noted that equation (6.108) is the same as equation (4.421), and that these are simpler than the expression for $\Delta''_{av}$ because in the latter case the starting value of $\Delta$ is not given.

## §2. Conclusion.

Returning now to the matter of Chapter I, §5, we are in a position to discuss the various points of the Ehrenfests' programme and to compare them with our results. We take them separately.

(1) If H' is much larger than H then the H-curve will practically always decrease from H'. This is true since

$(dH/dt)_{av}$ is negative, and the larger is H' the more pronounced is the decrease [equation (4.422)]. The process is reversible with time. This was proved in the preceding section. The system will spend the majority of time in the equilibrium state. The form of w(H,H') [equation (5.202)] shows that the most probable transitions are those in which the change in H is small, and also where such values of H are themselves near the equilibrium value. Therefore the majority of the fluctuations will be small ones around the equilibrium value, and the system will spend most of the time at least in the neighbourhood of the equilibrium state. The equilibrium distribution is given by the Maxwell-Boltzmann distribution of equation (4.308).

(2) Any value of H may occur again and again, and yet the system will appear to be irreversible. The expression obtained for the recurrence probability showed that any value of H has a finite probability of recurrence. However the mean recurrence times of large values of H are so vast in comparison with the times available for observation that the likelihood of observing such a recurrence is exceedingly small. In this way any observation is likely to show a rapid approach to the equilibrium state in which the system will then remain, apart from possible very small fluctuations.

(3) The $\bar{H}$-curve formed by the ensemble averages of H is the same as the H-theorem curve. The dispersion of H values around the mean given by $\bar{H}$ is very small, so that most of the curves of H with time for the members of the ensemble follow the H-theorem curve values. Thus again we may say that the likelihood of observing deviations from this average behaviour is very small.
(4) The Poincaré period is exceedingly long, of the order of the recurrence time of the state $H_{max}$. The relaxation times on the other hand are short, and become shorter if larger cells are chosen in phase space. The rate of decrease of H depends upon the quantity A, which is a constant for each model. The results are otherwise general for this class of model, but in each case we have that A is of the same, very small, order of magnitude. This is important because of the many expressions which have been derived approximately to the first order in A.

We have thus confirmed each point in the Ehrenfests' programme as it applies to this class of simple models. The main assumptions which we have made were discussed in Chapter V, and we found that if they were not rigorously justified yet there was at least a high degree of plausibility attached to them. The methods used will be found to have parallels elsewhere in statistical

mechanical work, which by its nature must rely to a great extent upon the plausibility of the results to justify the methods used. It seems however, that Bartlett's work in particular (Chapter V, §3) shows signs of being very important in this respect, and could perhaps be extended to justify more rigorously the assumptions which are commonly made concerning the previous history of the members of the ensemble. It was not to be expected that such an investigation as we have carried out should yield any new results apart from verifying previous assertions made concerning the behaviour of the H-curve in the only possible manner, that is by dealing with an actual system.

## Appendix

§1. The Method of Steepest Descents.

This method of approximately evaluating integrals involving the exponential function is well known, for example see Jeffreys and Jeffreys (1946, p.472). We will here give the result as it applies to real variables, and also a typical example of its use from Chapter V.

Suppose we have an integral of the form

$$I = \int_A^B \chi(x)\, e^{t.f(x)}\, dx \qquad (A.101)$$

where t is large and positive. Then if f(x) has a maximum at $x = x_o$, so that $f'(x_o) = 0$, we may write the approximate value of I as

$$I = \sqrt{2\pi}\ \chi(x_o) e^{t.f(x_o)} \left| t.f''(x_o) \right|^{-\frac{1}{2}} . \qquad (A.102)$$

As an example we take the integral from equation (5.205):

$$I = \int_{H_{min}}^{\infty} H' [8\pi A(H-H_{min})]^{-\frac{1}{2}} e^{-[H'-H+2A(H-H_{min})]^2/8A(H-H_{min})} dH' , \qquad (A.103)$$

where A is very small as compered to unity. Thus we may take t as 1/A, and we have for the functions in equation (A.101) the expressions

$$f(H') = [H'-H+2A(H-H_{min})]^2/8A(H-H_{min}) , \qquad (A.104)$$

and

$$(H') = H'[8\pi A(H-H_{min})]^{-\frac{1}{2}} \quad . \qquad (A.105)$$

From equation (A.104) it follows that $f'(H') = 0$ if

$$H'_o = H-2A(H-H_{min}) \quad , \qquad (A.106)$$

while

$$f''(H'_o) = [4(H-H_{min})]^{-1} \quad . \qquad (A.107)$$

Thus from equation (A.102) we have the approximate value of I to the first power in A as

$$I = 2\pi[H-2A(H-H_{min})][8\pi A(H-H_{min})]^{-\frac{1}{2}}[4A(H-H_{min})]^{\frac{1}{2}}$$

$$= (1-2A)(H-H_{min}) + H_{min} \quad . \qquad (A.108)$$

§2. A Contour Integration.

Two somewhat similar contour integrations arise from the calculations in Chapter III. The first is from equation (3.309). Suppose that I is the integral

$$I = \int_{-\infty}^{+\infty} (1-i\rho)^{-3/2} e^{-i\rho\Delta}\, d\rho \quad . \qquad (A.201)$$

Writing $\xi = i\rho - 1$ as a new variable, we see that as $\rho$ goes along the real axis from $-\infty$ to $+\infty$, then $\xi$ moves along a line through the point $-1$ and parallel to the imaginary axis from $-i\infty$ to $+i\infty$, so that we have

$$I = (-i) \int_{-1-i\infty}^{-1+i\infty} (-\xi)^{-3/2} e^{-\Delta(\xi+1)}\, d\xi \quad . \qquad (A.202)$$

We now take a contour as shown in figure 5. There

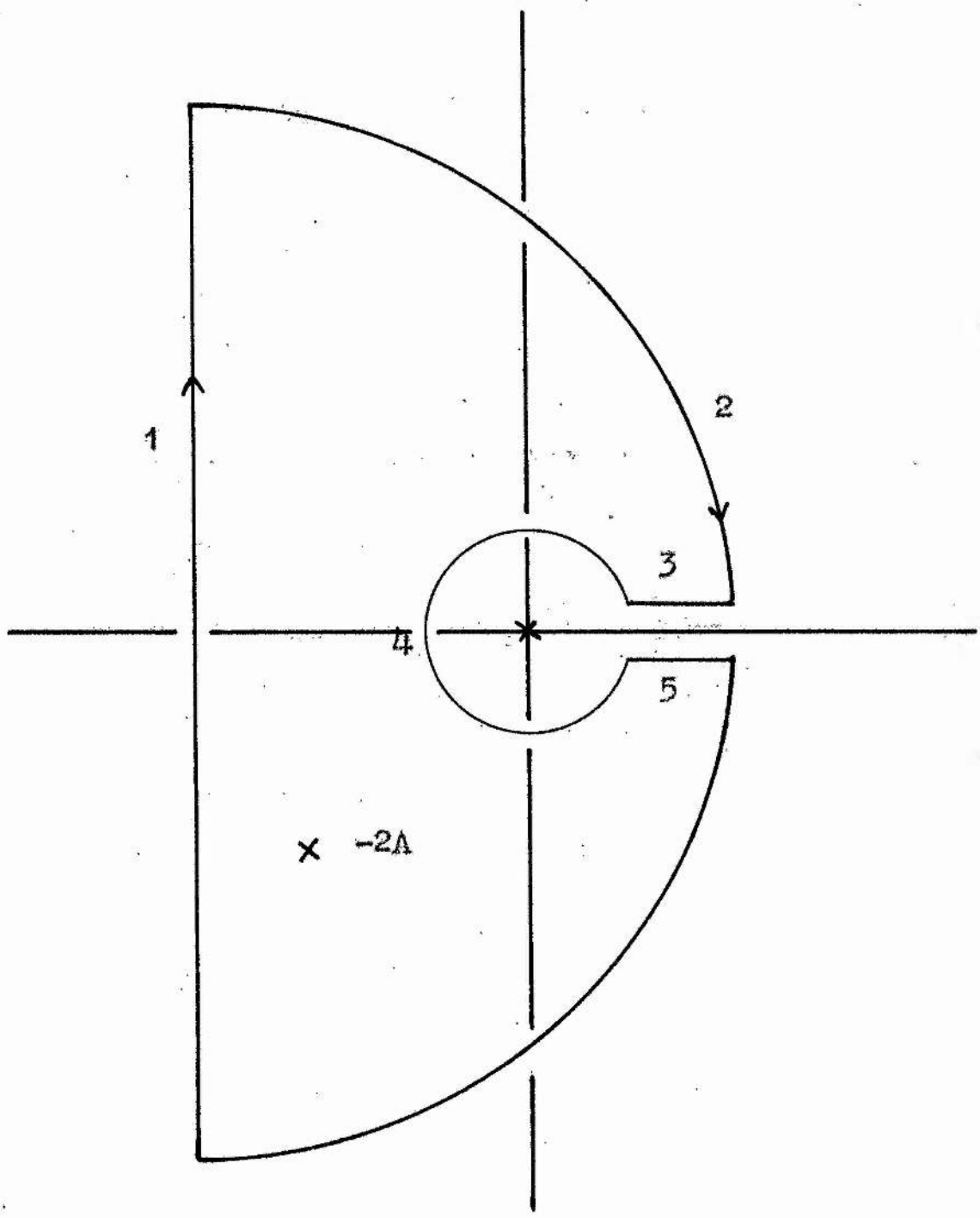



Figure 5

is a branch point at the origin. If the radii of the two circular contours are R and r , (R > r), it is easily shown that the integrals around these vanish as $R \to \infty$ and $r \to 0$. Denoting the integral along the contour 3 by J, then

$$J = -\lim_{\substack{r\to 0 \\ R\to\infty}} \int_{r}^{R} i(-\xi)^{-3/2} e^{-\Delta(\xi+1)} d\xi \quad . \qquad (A.203)$$

Upon taking the Cauchy principal value and also the limits we obtain the factorial function

$$J = \int_{0}^{\infty} x^{-3/2} e^{-\Delta(x+1)} dx$$

$$= e^{-\Delta}\, \Delta^{\frac{1}{2}} (-3/2)! \quad . \qquad (A.204)$$

Therefore

$$I = -2J = 4(\pi\Delta)^{\frac{1}{2}}\, e^{-\Delta} \quad , \qquad (A.205)$$

and hence equation (3.310) for $w(\Delta)$.

## §3. Another Contour Integration.

This integral arises from the evaluation of $w(\Delta)w(\Delta,\Delta')$ in Chapter III [equation (3.318)]. We have there the integral

$$I = \int_{-\infty}^{+\infty} (4A - i\sigma + 1)^{-\frac{1}{2}} (2A - i\sigma + 1)^{-1} e^{-i\sigma\Delta} d\sigma \quad , \qquad (A.301)$$

where A is constant.

As before we take the new variable $\xi$ where now $\xi = i\sigma - a$, and $a = 4A + 1$. Therefore I becomes

$$I = (-i) \int_{-a-i\infty}^{-a+i\infty} (-\xi)^{-\frac{1}{2}} (-2A - \xi)^{-1} e^{-\Delta(\xi+a)} d\xi \quad . \qquad (A.302)$$

The contour illustrated in figure 5 is still suitable, but now in addition to the branch point at the origin there is a simple pole at $-2A$, which is inside the contour. Suppose that $J$ denotes the integral along the contour 3. The integrals over the circular contours vanish as before. Then

$$J = -\lim_{\substack{r\to 0 \\ R\to\infty}} \int_{R}^{r} i(-\xi)^{-\frac{1}{2}}(2A+\xi)^{-1}e^{-\Delta(\xi+a)}d\xi \quad , \qquad (A.303)$$

and, taking the principal value and the limits;

$$J = \int_{0}^{\infty} x^{-\frac{1}{2}}(2A+x)^{-1}e^{-\Delta(x+a)}dx \quad . \qquad (A.304)$$

Therefore

$$I = -2J - 2\pi i \text{ (residue at } -2A)$$

$$= -2J + 2\pi(2A)^{\frac{1}{2}}e^{-\Delta(2A+1)} \quad . \qquad (A.305)$$

After integrating equation (A.304) by parts twice we obtain the relation for $J$

$$J = 2e^{-a\Delta}\left[e^{a\Delta}J - 2A\int_{0}^{\infty} x^{-\frac{1}{2}}(2A+x)^{-2}e^{-x\Delta}\,dx + \Delta\int_{0}^{\infty} x^{-\frac{1}{2}}e^{-x\Delta}\,dx - 2A\Delta\, e^{a\Delta}J\right] \quad . \qquad (A.306)$$

It may be seen on inspection that $J$ satisfies the partial differential equation

$$\frac{\partial J}{\partial A} + \left(\frac{1}{2A} + 2\Delta\right)J + \frac{\sqrt{\pi\Delta}}{A}e^{-a\Delta} = 0,$$

with the solution

$$J = -(\pi\Delta/A)^{\frac{1}{2}}e^{-2\Delta(A+\frac{1}{2})}\left[\int_{0}^{A} A^{-\frac{1}{2}}e^{-2A\Delta}\,dA - k\right] . \qquad (A.307)$$

The constant k follows from the boundary condition that $J(\infty) = 0$, and so we have for I the result

$$I = (2/\Lambda)^{\frac{1}{2}} \mathrm{erf}[(2\Lambda\Delta)^{\frac{1}{2}}]\, e^{-2\Delta(\Lambda+\frac{1}{2})} \quad , \qquad (\Lambda.308)$$

where erf denotes the error function

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad . \qquad (\Lambda.309)$$

See, for example, Jahnke and Emde (1933, p.97). It is shown there that for $x \ll 1$ we may use the series expansion

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\left[x - \frac{x^3}{1!3} + \frac{x^5}{2!5} - \ldots\right] \quad . \qquad (\Lambda.310)$$

In order to obtain $w(\Lambda)w(\Lambda,\Lambda')$ it is necessary to evaluate the integral K, where

$$K = \int_{-\infty}^{+\infty} I\, e^{-i\varsigma\delta\Delta} d\varsigma \quad , \qquad (\Lambda.311)$$

and I has the value given by equation (Λ.308), and the expression for Λ in that equation is given as a function of $\varsigma$ by

$$A = 2g(i\varsigma + \varsigma^2) \qquad [3.315] \quad .$$

The form of the integrand ensures that it will only have significant magnitude when $\varsigma$ is small, so that we may use the approximation (A.310) for erf(x). Thus, substituting $(2A\Delta)^{1/2}$ for $\mathrm{erf}[(2A\Delta)^{1/2}]$ in the expression for I we obtain

$$K = \int_{-\infty}^{+\infty} 2\pi\, \Delta^{\frac{1}{2}} e^{-\Delta - 4g\Delta(i\varsigma+\varsigma^2)} d\varsigma \qquad (\Lambda.312)$$

which, when evaluated, gives the result expressed in equation (3.321).

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